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THE UNIVERSITY OF ALBERTA

STUDY OF IRON(II) and IRON(III) IN ACETONITRILE

by



ROBERT ARTHUR LONG

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

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UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and  
recommend to the Faculty of Graduate Studies for acceptance,  
a thesis entitled STUDY OF IRON(II) AND IRON(III) IN  
ACETONITRILE  
submitted by ROBERT A. LONG  
in partial fulfilment of the requirements for the degree of  
Doctor of Philosophy.



ABSTRACT

A study of oxidation-reduction and complexation of anhydrous iron(III) and iron(II) in acetonitrile, and an investigation of the scope of hydrated iron(III) perchlorate as an analytical oxidant, has been made. The formal reduction potential of the anhydrous iron(III)-(II) couple in acetonitrile at iron(II) and iron(III) concentrations of  $2 \times 10^{-3} \text{M}$  is  $1.57 \pm 0.05 \text{ V}$  vs. the silver,  $0.01 \text{M}$  silver nitrate in acetonitrile reference electrode. Anhydrous iron(III) perchlorate was generated in solution by electrolytic oxidation of anhydrous iron(II) perchlorate. It was found to be extremely hygroscopic and easily hydrolyzed by traces of water.

Iron(II) forms stable 1:1 complexes with chloride, bromide, iodide and both 1:1 and 1:2 complexes with thiocyanate in acetonitrile. Stepwise formation constants for the complexes were determined spectrophotometrically by a mole ratio method. The log K values are:  $\text{FeCl}^+$ , 5.8;  $\text{FeBr}^+$ , 5.5;  $\text{FeI}^+$ , 4.3;  $\text{Fe(SCN)}^+$ , 5.5; and  $\text{Fe(SCN)}_2$ , 3.7. Qualitative evidence for strong iron(III) complexation with these anions was also found.

The scope of hydrated iron(III) perchlorate in acetonitrile as an analytical oxidant was investigated. Among the compounds quantitatively oxidized are several benzidines, ferrocenes,



hydroquinone, tetrachlorohydroquinone, thiocyanate, iodide, phenothiazines, and N,N'-diphenyl-p-phenylenediamine. In general, the criteria for clean oxidation are the presence of an electronegative site such as an oxygen, nitrogen, or sulfur atom and the ability of the oxidized species to form resonant stabilized structures. Compounds such as the thiols are oxidized but give unstoichiometric titration plots. The principal disadvantage of hydrated iron(III) perchlorate as a titrant is hydrolysis by water, which makes daily standardization necessary and which makes the titrant molarity vary with the reduction potential of the compound being oxidized.



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PART I.

INTRODUCTION

Since the beginning of chemistry, convenience and ease of handling have made liquids the preferred media in which to carry out chemical reactions. Of all liquids, water, with its availability, high dielectric constant, high donor number, and ease of purification and handling, has been the solvent of choice. However, water is incompatible with or unsatisfactory for use with many reagents, and chemists therefore turned to nonaqueous solvents, both organic and inorganic. Nonaqueous solvents are now being used extensively for a variety of practical analytical applications. However, until the last few years little work has been done on the fundamental aspects of these systems.

Water, with all its generally useful qualities, has several specific disadvantages. It may act as a source of hydroxyl ions to cause unwanted hydrolysis, or may react with or precipitate reaction intermediates such as free radicals. Being very polar, it does not dissolve most nonpolar organic compounds or salts of large cations and large anions. It has a pronounced leveling effect on strong acids and bases. For these reasons, among others, nonaqueous solvents are seeing increased study as media for particular systems.

Solvents other than water are also playing an important



role in the field of coordination chemistry. Previously unknown complexes often can be prepared readily when complications such as hydrolysis are avoided and ligand-solvent competition is changed. Limited work in this area has permitted several generalizations to be made about complexation in nonaqueous solvents. First, the reactivity of a cation toward complexation depends more on electron donating properties of the solvent than on its dielectric constant; donating strengths of a number of solvents have been tabulated according to arbitrary donor numbers<sup>1</sup>. Second, cations can be roughly divided into two groups depending on whether they complex most strongly with the first anions in each group of the periodic table or with subsequent members of the group (concept of hard and soft acids<sup>2</sup>). These generalizations, though resting on a tentative theoretical foundation, can give a good a priori idea of what to expect in a solvent other than water.

Within the field of nonaqueous solvents the area of acid-base reactions has been the most thoroughly studied and broadly applied. In fact, with the exception of some polarographic work, analytical research in nonaqueous solvents has been almost entirely limited to this area. This interest in acid-base reactions is well deserved from a practical point of view, because many useful compounds such as pharmaceuticals exhibit acid-base properties which are too weak for titration in water



but which can be enhanced sufficiently by other solvents to permit their determination. From the wide variety of solvents available, one can usually be picked which has the desired acid-base properties for a particular system.

Although acid-base reactions have been well studied, the field of electron transfer or oxidation-reduction reactions in nonaqueous media has barely been touched. Michaelis and Hill<sup>3</sup> found that substances such as N,N'-diphenyl-p-phenylenediamine, which are only slightly soluble in water, could be dissolved and titrated in 90% acetic acid-water mixtures. Several other workers studied oxidation-reduction reactions in anhydrous acetic acid using common aqueous titrants such as cerium(IV) sulfate, permanganate, bromine, etc., but found that these reactions were of limited utility because of slow reaction rates and uncertain equivalence points<sup>4-6</sup>. Ion association and the resulting lack of ionic species slowed reaction rates and indicated the need for a solvent of higher dielectric constant to promote dissociation. Although several solvents have this characteristic, acetonitrile has been the most extensively studied.

The properties of acetonitrile are listed in Table I. The moderate dielectric constant makes it suited for dissolving nonpolar organic compounds as well as many metal salts of large, symmetrical anions such as the perchlorates,





TABLE I. - Physical Properties of Acetonitrile and Water

Property	Acetonitrile	Water
Boiling Point (°C)	81.60 <sup>7</sup>	100
Freezing Point (°C)	-45.72 <sup>7</sup>	0
Dielectric Constant 0°C:	42.0 <sup>8</sup>	-
20°C:	38.8 <sup>8</sup>	-
25°C:	36.0 <sup>8</sup>	78.54
Density (g cm <sup>-3</sup> @ 25°C)	0.7767 <sup>9</sup>	0.9971
Viscosity (centipoise at 25°C)	0.345 <sup>9</sup>	8.937
Donor Number (DN <sub>SbCl<sub>5</sub></sub> )	14.1 <sup>1</sup>	18.0 <sup>1</sup>
Dipole Moment (Debye)	3.37 <sup>7</sup>	1.84
Trouton-Constant (cal mole <sup>-1</sup> deg <sup>-1</sup> )	22.09 <sup>10</sup>	25.92
Heat of Vaporization at boiling point (Kcal/mole)	7.127 <sup>7</sup>	9.72
Spectral cut-off wavelength in ultraviolet (millimicrons)	189 <sup>11</sup>	below 189
Potential at which oxidized*	2.3 V <sup>11**</sup>	1.8 V <sup>**</sup>
Potential at which reduced***	-2.7 V <sup>11**</sup>	-2.3 V <sup>**</sup>
Autoprotolysis Constant	3 × 10 <sup>-29</sup> <sup>12</sup>	1 × 10 <sup>-14</sup>
Vapor Pressure (mm Hg @ 25°C)	89.0 <sup>7</sup>	23.756

\* NaClO<sub>4</sub> supporting electrolyte with platinum electrode.

\*\* vs. aqueous SCE.

\*\*\* Tetraethylammonium supporting electrolyte with mercury electrode.



tetrafluoroborates, and hexafluorophosphates. The common salts used in water are in general sparingly soluble in acetonitrile. A donor number of 14.1<sup>1</sup> places it midway between 1,2 dichloroethane ( $\text{DN}_{\text{SbCl}_5} = 0$ ) and dimethylsulfoxide ( $\text{DN}_{\text{SbCl}_5} = 29.8$ ) and allows the formation of a number of complexes. The stability of acetonitrile toward oxidation-reduction is better than that of water, and allows the use of powerful oxidizing and reducing titrants. Several methods of purification have been developed so that pure acetonitrile can be prepared. These properties, along with only moderate toxicity and ease of handling, make it an almost ideal solvent for oxidation-reduction work.

The toxicity of acetonitrile<sup>13</sup> is worth mentioning briefly. Tests on animals show that it has a moderate toxicity due to slow hydrolysis in the body to cyanide. 40 ppm has been set as the tentative threshold limit of toxicity. In all cases precautions should be taken to minimize exposure to both the vapor and liquid, especially old impure grades which often contain some HCN.

Kolthoff and Coetzee were the first to survey oxidation-reduction reactions in acetonitrile systematically. A preliminary survey<sup>14,15</sup> was made of the behavior of the alkali metals, alkaline earth metals and many of the transition metals polarographically at dropping mercury and at rotating platinum



microelectrodes. In this investigation the metals fell into two classes, those toward which acetonitrile acted as a weak Lewis base and those that underwent specific interaction with acetonitrile. The first class consisted of the alkali and alkaline earth metals, and the second of transition metals such as Ag(I) and Cu(I). These papers serve as a useful guide to choosing reagents for study in oxidation-reduction reactions in acetonitrile.

Rao and Murthy<sup>16-18</sup> were the first investigators to use acetonitrile extensively for analytical electron transfer reactions. They found that ammonium hexanitratocerate was a good oxidant; the reduction potential of the hexanitratocerate-cerium(III) couple is 0.755 V vs. the silver reference electrode<sup>19</sup>. However, oxidation reactions using this reagent were often slow. They also found that the potential could be increased by addition of acetic acid and that in addition to increasing the potential, acetic acid, acetate, or picrate also increased reaction rates. Hydroquinone, iodide, ascorbic acid, oxalic acid, xanthate, and iron(II) were titrated. Unfortunately the composition of the solvent was not well specified, and therefore the results cannot be interpreted in terms of solvent effects.

Recently copper(II) perchlorate has been found to be a useful oxidant in acetonitrile<sup>20-23</sup>. The standard reduction



potential is 0.800 V vs. the silver reference electrode<sup>24</sup>.

This potential is higher than that seen in water because of relative stabilization of copper(I) by acetonitrile complexation. The titrant is stable and easy to prepare, use and standardize<sup>23</sup>. At the present time it is the most convenient titrant available for oxidations in acetonitrile. Unfortunately the potential is not high enough to be useful for the oxidation of many organic compounds.

In a search for a stronger titrant, the polarographic data of Coetzee<sup>14,15</sup> was reviewed and iron(III) chosen for investigation. The oxidation-reduction and complexation behavior of iron(II) and iron(III) in acetonitrile was studied and the scope of iron(III) as an analytical oxidant was investigated.





## PART II. THE IRON(III)-(II) COUPLE IN ACETONITRILE

### BACKGROUND

The reduction potential for any half reaction in a given solvent depends on several factors; in aqueous solutions pH, ionic strength, and the presence of complex forming species all affect the values observed. In a nonaqueous solvent, variations in these factors may produce even greater effects than are seen in water, especially if the solvent has a low dielectric constant which promotes ion association. In addition, specific ion solvation varies with the nature of the solvent. The net result is that potential differences between any two half reactions tend to vary appreciably on going from one solvent to another.

In general, reduction potentials in acetonitrile follow a predictable trend relative to those in water if one takes into account the fact that acetonitrile is a weaker Lewis base than water. In an early survey of polarography in acetonitrile, Kolthoff and Coetzee<sup>14</sup> found that the half wave reduction potentials for the alkali metals, alkaline earth metals, and several of the transition metals were lower than in water. In these cases the metal ions are less stabilized by acetonitrile solvation and are easier to reduce.



In a second paper Kolthoff and Coetzee pointed out that the reduction potentials for silver(I) and copper(I) indicated that they undergo specific solvation in acetonitrile<sup>15</sup>. In these cases coordination is strong enough that acetonitrile complexes of the metals can be isolated even in the presence of 0.1-0.2% water. Stabilization of the reduced species results in increased reduction potentials for the copper(II,I) and silver(II,I) systems in acetonitrile over those found in water.

Kolthoff and Coetzee also reported briefly on the iron(III,II) couple. At a rotating platinum micro-electrode, hydrated iron(III) perchlorate is reduced at a half wave potential of +0.8 V vs. the silver, 0.01M silver nitrate in acetonitrile reference electrode (hereafter called the silver reference electrode) and hydrated iron(II) perchlorate is oxidized at a half wave potential of +1.3 V vs. the silver reference electrode. Using the rubidium(I,0) couple as a reference system<sup>25</sup> to compare potentials, the values in acetonitrile are 0.5 to 1.0 V higher than those found in water. In addition to having a high reduction potential, the couple was very irreversible, as shown by the large difference in oxidation and reduction half wave potentials. The fact that these two properties (reduction potential and



reversibility) were so affected by the nature of the solvent indicates extensive interaction. Therefore a potentiometric study of solutions of anhydrous iron(II) and iron(III) perchlorate in acetonitrile was undertaken to provide information about some of the interactions observed between the solvent and iron solute.



## EXPERIMENTAL

### Reagents and Apparatus. Acetonitrile Purification.

Acetonitrile was purified by an adaptation of the method of O'Donnell, Ayres and Mann<sup>11</sup>. Technical grade acetonitrile (Matheson, Coleman and Bell, Norwood, Ohio) (about 2.5 liters per batch) was distilled rapidly from 30 ml of benzoyl chloride. The distillate was redistilled from 30 g of sodium carbonate and 5 ml of H<sub>2</sub>O to destroy any remaining benzoyl chloride, then redistilled again from 35 g of potassium permanganate and 35 g of sodium carbonate. This distillate was acidified with several drops of concentrated sulfuric acid to precipitate ammonia formed in the previous step, vacuum distilled rapidly, then distilled again at a high reflux ratio in a 30-plate column at 10 ml per hour. The first liter and the last 200 ml were discarded. Solvent purified in this way showed no absorption in the ultraviolet above 200 millimicrons, and no oxidizable impurities could be detected polarographically at +2.0 V vs. a silver-0.1M silver nitrate in acetonitrile reference electrode. Karl Fischer titrations showed the water content to be in the range of 1 to 2 x 10<sup>-4</sup>M. In those cases where even this amount interfered, acetonitrile prepared as outlined above was stirred with calcium hydride and filtered in a dry box immediately before use; in this way





a concentration of water less than  $5 \times 10^{-5} \text{M}$  was achieved.

Preparation of Metal Salts and Solutions. Hydrated iron(II) perchlorate was prepared from perchloric acid and electrolytic iron. Hydrated iron(III) perchlorate (non-yellow, with excess perchloric acid) was used as received (G. F. Smith Chemical Co., Columbus, Ohio, and Alfa Inorganics, Beverly, Mass.). Anhydrous silver perchlorate was prepared by reacting silver carbonate with a slight excess of perchloric acid, evaporating, filtering and drying in a high vacuum at about  $60^\circ\text{C}$ .

Anhydrous iron(II) perchlorate,  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{CH}_3\text{CN}$ , was prepared by azeotropic distillation of solutions of hydrated iron(II) perchlorate in acetonitrile under reduced pressure in the presence of Linde 3A molecular sieves, followed by removal of the excess solvent in a vacuum at room temperature. The final product, white with a pale blue-green cast, is stable in the dry state to  $125^\circ\text{C}$ . Above this temperature it decomposes slowly on heating in a capillary tube, or explosively if thrown on a hot plate at  $200^\circ\text{C}$ . Solutions of the iron(II) salt in acetonitrile are stable to at least  $50^\circ\text{C}$ . (Note: Caution should be exercised in heating solutions of perchlorate salts in organic solvents. Safety precautions must always be taken.) Analysis of the salt by titration in aqueous solution with potassium dichromate gave a purity of 100.3%. The slightly high value is



probably caused by the loss of some coordinated acetonitrile upon drying in a vacuum.

Attempts to prepare anhydrous iron(III) perchlorate,  $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{CH}_3\text{CN}$ , by metathesis were performed in two ways. Stoichiometric quantities of the following compounds were combined: (Trial 1) 30 ml of 1M anhydrous iron(III) chloride (Fisher anhydrous reagent) in dry acetonitrile were added dropwise to 30 ml of a vigorously stirred 3M solution of anhydrous silver perchlorate. (Trial 2) 30 ml of a solution 3M in anhydrous barium perchlorate and 1M in anhydrous iron(III) chloride were added dropwise with stirring to a suspension of 90 millimoles of anhydrous silver sulfate in 50 ml of dry acetonitrile. All work was carried out in a dry box with the exception of the evaporations, when the solutions were transferred without contact with the room atmosphere to a vacuum rack. The resulting solution was evaporated almost to dryness, the silver chloride or barium sulfate filtered off, and the solution evaporated further. A bright red solution, having the characteristic spectrum of iron(III)-chloro complexes, was recovered in each case. Addition of excess silver perchlorate did not eliminate the red color of the chlorocomplexes.

Several procedures for dehydrating commercial iron(III) perchlorate were also attempted. In the first, 200 ml of acetic anhydride (Fisher certified ACS grade) were added dropwise



with vigorous stirring to 50 ml of 0.1M hydrated iron(III) perchlorate in technical grade acetonitrile. A safety shield was employed. The temperature was kept below 35°C during the addition, which required about 2½ hours. Immediately after the addition was complete the excess acetonitrile and acetic acid were removed under a high vacuum at room temperature and the products allowed to slowly crystallize from the acetic anhydride overnight. A mixture of black needle-like crystals and light green cubic crystals resulted in each case.

Determinations of the iron content indicated these products were iron(III) and iron(II) perchlorate, respectively, with acetonitrile, acetic acid and/or acetic anhydride present in each case. Rough potential measurements were made on the black needles of the iron(III) salt by reduction of approximately 50% of the iron(III) with ferrocene and measurement of the resulting potential with an Orion digital pH meter, using a platinum-silver reference electrode pair. Values in the range of +1.3 to +1.5 V vs. the silver reference electrode were found. Three other attempts at this synthesis using increased concentrations of iron(III) perchlorate, using cooled solutions, and eliminating the vacuum evaporation step gave in all cases decreased yields of the iron(III) salt. Because of the large amounts of iron(II) salt formed in each case (sometimes over 90%) the method was abandoned.



A dehydration using distillation of N,N'-dimethylauramide (DML) - water azeotrope according to a method used in other solvents by C. A. Reynolds<sup>26</sup> was also tried. N,N'-dimethylauramide (DML) (C. P. Hall Co., Chicago, Illinois) was vacuum distilled from sodium hydroxide pellets. 40 g of hydrated iron(III) perchlorate was mixed with 600 mls of purified DML, then stirred at room temperature for several days under a vacuum of 0.005 microns. During this time the azeotrope was collected in a liquid nitrogen cold trap. A yellow gelatinous mass, presumably  $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{DML}$ , was obtained. Treatment with acetonitrile did not yield the desired acetonitrile adduct. A crude potential measurement on this species, similar to that described for the product of the dehydration with acetic anhydride, gave a potential of about +0.6 V vs. the silver reference electrode.

Dehydrations of hydrated iron(III) perchlorate with 2,2-dimethoxypropane or triethylorthoformate were not tried because of the potential safety hazard. It was felt that explosive perchlorate esters might form from the presence of excess perchloric acid and alcohols, produced as by-products of the dehydrations, in the same solution.





Electrochemical oxidation turned out to be the best way to prepare solutions of anhydrous iron(III) perchlorate from iron(II) perchlorate; however several modifications to conventional aqueous apparatus were necessary for satisfactory results. Initial electrolyses were run in a glass H-cell with two 1-cm diameter ultrafine frits and a 0.1M lithium perchlorate salt bridge separating the cathode and anode compartments. The anode compartment contained 0.1M iron(II) perchlorate and the cathode compartment a saturated silver perchlorate solution. All solutions were prepared from dry acetonitrile and all operations were carried out in a dry box. The cell resistance was only 200 ohms at 1000 Hz measured with a General Radio impedance bridge, but rose to more than 3000 ohms when a 6 mA D.C. current was passed. The large resistance was due to concentration polarization effects across the frits. The resulting IR drop caused heating and mixing problems.

A cell in which the ultrafine frits were replaced by porous vycor tubing was also tried. It consisted of a 1-cm diameter porous vycor tube fastened to the bottom of a tall 10-cm diameter weighing bottle with Dow Corning silicone cement. This cell had an A.C. resistance of only 45 ohms, but a resistance of 5,500 ohms to a 5-mA D.C. current. Due to the high D.C. resistance this cell also had to be rejected.

A third cell dividing material, an ion exchange membrane,



was also investigated. These membranes have not previously found much application to nonaqueous electrolysis or coulometry. They consist of styrene graft-polymerized on a polyethylene or polymeric fluorocarbon backbone, and have the highly desirable properties of low resistance, chemical inertness, low porosity and high permselectivity<sup>27</sup>. Resistance measurements of these membranes, using 0.01M  $\text{LiClO}_4$  in acetonitrile on each side, gave values of about 10 ohms/cm<sup>2</sup> at 1000 Hz and 2,500 ohms/cm<sup>2</sup> for 6mA D.C. currents. The membranes are insoluble in acetonitrile, but become brittle after about six months of continuous immersion in acetonitrile. They are inert to most strong oxidants and have a low porosity. In fact, the permeability to acetonitrile at a head of several feet is less than the evaporation rate at the surface, for no wetting could be detected on the outer surface. Finally, the permselectivity of these membranes is very high. Permselectivity refers to the contrasting permeability of the membrane to ions of different charge. For example, a cation exchange membrane will allow cations to pass approximately  $10^4$  times faster than anions<sup>27</sup>. These properties make the membranes ideal for electrolysis and coulometry, where mixing between cathode and anode compartments must be minimized. They are especially useful in nonaqueous solvents, where solution resistances are normally much higher than in water and where



solvent viscosities may be lower. The first cell design employing this material as a separator was a flow through type; it consisted of a membrane sandwiched between two hemispherical compartments machined from nylon. The solutions were pumped through the compartments by peristaltic pumps using Dow Corning Silastic silicone rubber tubing. Oxidation was occurring, as evidenced by the formation of a red iron(III) hydroxy species in the iron(II) compartment, but the hydroscopicity of the iron(III) salt, combined with the permeability of the nylon to water vapor, allowed uptake of water and subsequent hydrolysis of the iron(III).

A more satisfactory design is shown in Figure 1. Glass cathode and anode compartments were separated with about 6 cm<sup>2</sup> of an anion exchange membrane in the perchlorate form. The membrane (AMF A104-EC, donated by American Machine and Foundry Co., Springdale, Conn.) had low resistance to D.C. currents on the order of 6 to 10 mA and low permeability to cations (no detectable silver ion diffusion was observed in 5 hours). The anion exchange membrane was placed between two silicone rubber gaskets, then between the two flanges of the cell. The unit was fastened together with a horseshoe clamp. The distance between the counter and working electrodes was kept as short as possible to minimize solution resistance. The counter electrode compartment contained 0.1M anhydrous silver



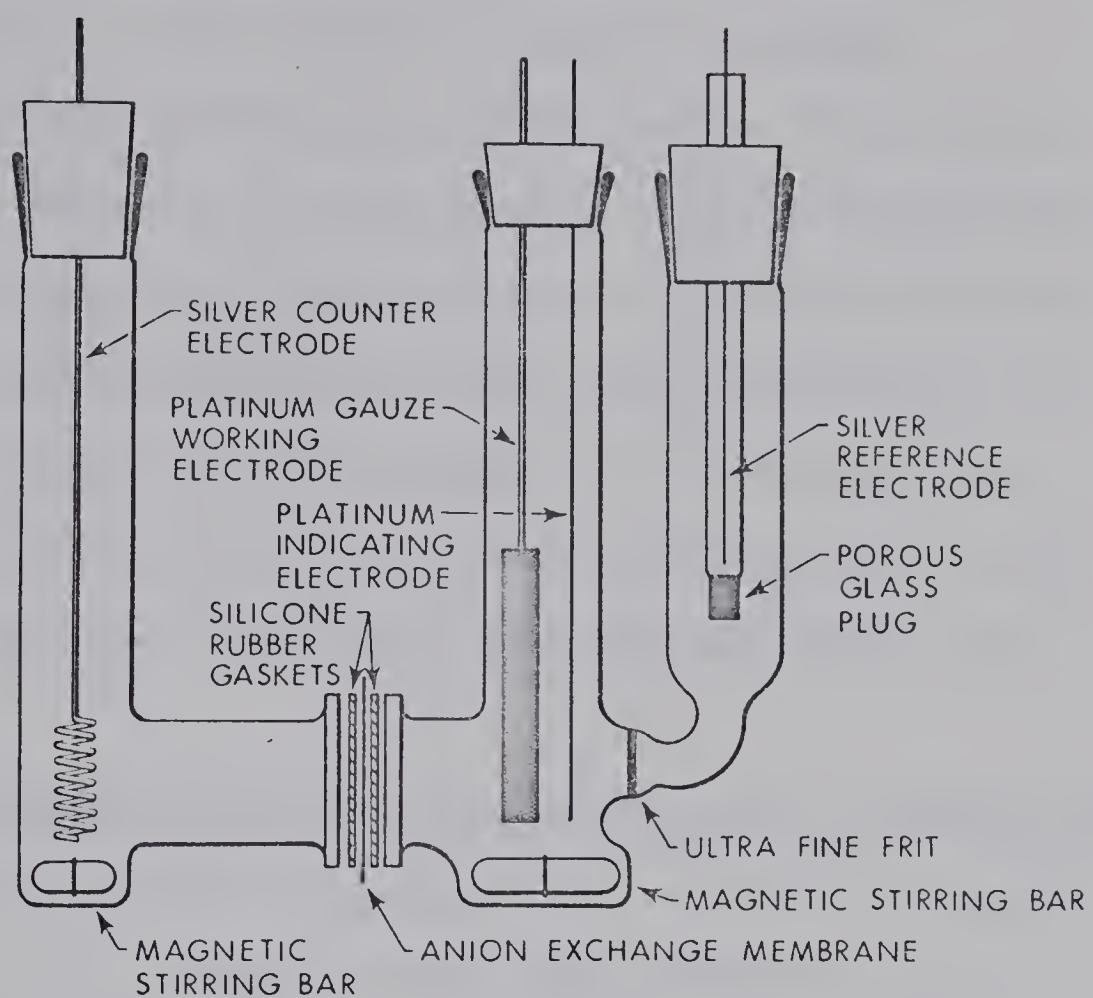


Figure 1. Electrolysis and coulometric H-cell with ion exchange membrane cell divider





perchlorate in dry acetonitrile. Perchlorate ions carried the current and readily migrated through the membrane. Solution volumes were kept low, on the order of 25 ml on each side of the membrane. By using a small volume of concentrated perchlorate solution, current efficiencies could be maintained at 100%, while the electrolysis times were held to about five hours. A Leeds and Northrup Coulometric Analyzer was used for the electrolyses; currents of 0.643 mA (occasionally 6.43 mA) were employed. 100% current efficiency was found in all cases.

#### Measurement of the Iron(III)-(II) Potential in Acetonitrile.

The reduction potential of the anhydrous iron(III)-(II) couple was measured in a stoppered glass H-cell (Figure 2) with a platinum foil indicating electrode and a  $1.00 \times 10^{-2}\text{M}$  silver nitrate in acetonitrile, silver foil reference electrode. The electrode compartments were separated by a  $0.1\text{M}$  tetraethylammonium perchlorate in acetonitrile salt bridge. An approximately  $9.4 \times 10^{-2}\text{M}$  solution of iron(II) perchlorate was electrochemically oxidized in a dry box as described previously to give about equimolar concentrations of iron(III) and iron(II), then diluted to  $2 \times 10^{-3}\text{M}$  in each constituent and transferred to the H-cell. The cell was removed from the dry box, placed in a water bath at  $25.00 \pm 0.05^\circ\text{C}$  and the potential measured with a Leeds and Northrup Type K4



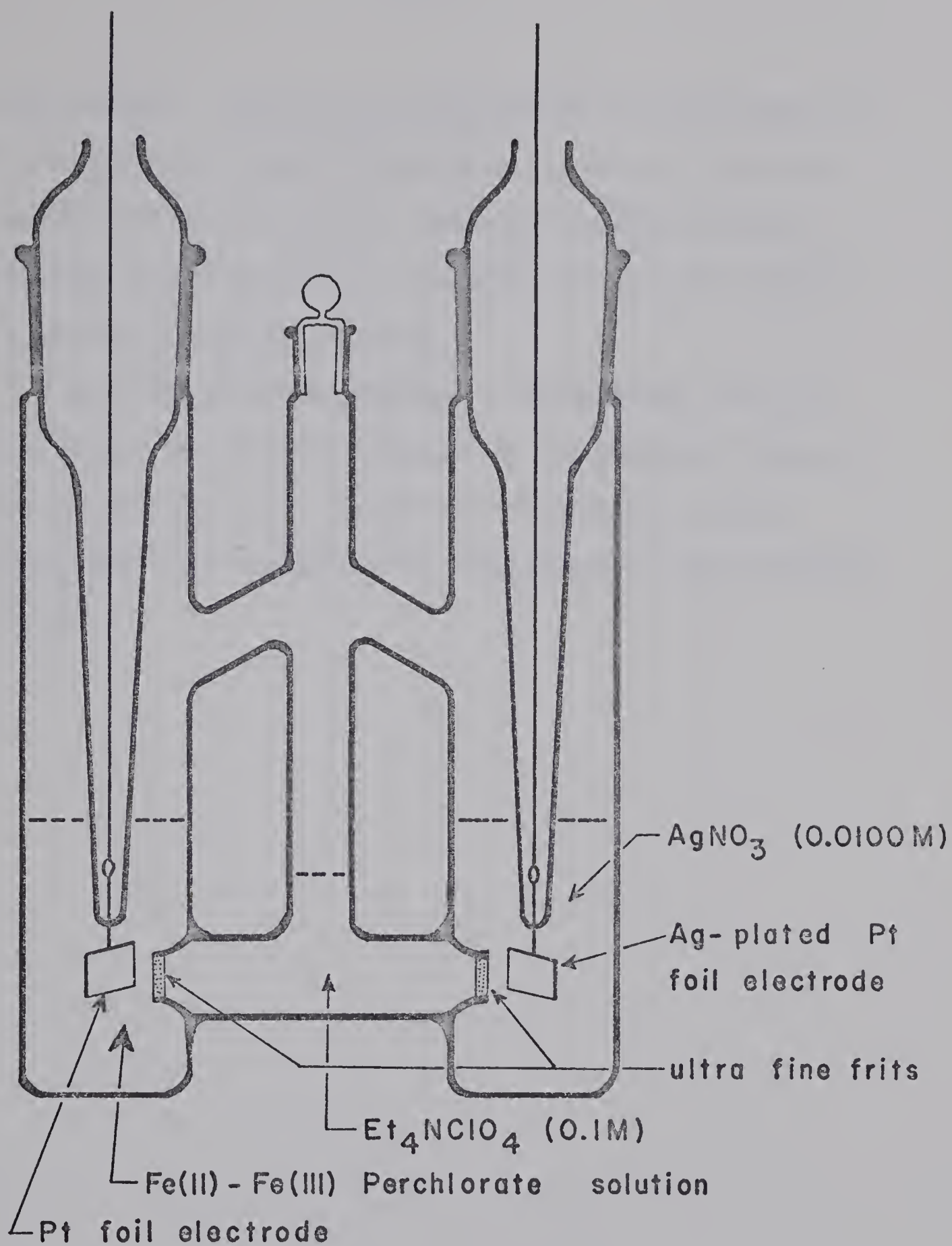


Figure 2. H-cell used in potential measurements



potentiometer. Hydrolysis of the iron(III) by trace water in the acetonitrile caused the potential to fall at a rate of several millivolts a minute. The value reported here was obtained by extrapolation of the potentials to zero time and is considered accurate to  $\pm 0.05$  V.

An estimate of the potential of the hydrated iron(III)-(II) couple was obtained by measuring the potential 100% past the equivalence point in iron(III) titrations of iodide, hydroquinone, and thiourea with a Metrohm Model 436E recording titrator.



## RESULTS AND DISCUSSION

### Anhydrous Iron(III)-(II) Couple in Acetonitrile.

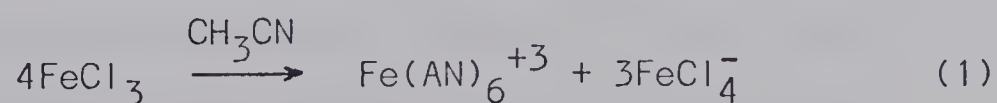
The formal reduction potential of the iron(III)-(II) couple in acetonitrile, measured at iron(II) and iron(III) concentrations of  $2 \times 10^{-3} \text{ M}$ , is  $1.57 \pm 0.05 \text{ V}$  vs. the silver reference electrode. The iron(III) was obtained by 50% oxidation of iron(II) perchlorate coulometrically under as dry conditions as possible. The oxidized solutions were yellow in all cases, the color gradually intensifying and the cell potential drifting downward with time. The color is caused by the visible tail of an absorption maxima at 359 millimicrons, and is characteristic of  $\text{Fe}(\text{OH})^{+2}$ ,<sup>28</sup> which would be expected to form from iron(III) reaction with traces of water in the solvent. The presence of this contamination prevented measurement of an accurate thermodynamic potential, and also affected the reversibility of the couple. However, the high formal potential value shows iron(III) to be a powerful oxidant in acetonitrile and provides an indication of the effects which may be produced upon changing from water to another solvent. Using the rubidium(I)-(0) couple as a reference system for comparing potentials between acetonitrile and water<sup>25</sup>, the increase in the iron reduction potential in acetonitrile over that in water is estimated to be 1.3 V.





This increase may be partly attributed to increased stabilization of iron(II), since the crystal field splitting energy for iron(II) in acetonitrile, measured spectrophotometrically by Hathaway and Holah, is some  $600\text{ cm}^{-1}$  greater in acetonitrile than in water<sup>29</sup>. Iron(III) destabilization is probably also important, however, for the lower dielectric constant of acetonitrile would not be expected to readily stabilize species of high charge.

The instability of the anhydrous iron(III)-acetonitrile complex, as indicated by the high reduction potential, probably explains why it was not possible to prepare the anhydrous iron(III) salt. The iron tends to either undergo complexation with a ligand other than acetonitrile (such as DML or hydroxide), or to reduce to iron(II). Thus, the metathesis reactions starting with iron(III) chloride, described earlier in the preparative section, could not be driven to completion because of the high stability of the iron(III) chlorocomplexes. Hathaway and Holah<sup>29</sup> found that the tetrachloroferrate complex is so strong that iron(III) chloride dissolved in acetonitrile undergoes the following solvolysis reaction:



Indeed, in the metathesis reactions attempted in this work



spectra of the resulting solutions gave maxima corresponding to that reported for  $\text{FeCl}_4^-$  even after evaporation almost to dryness.

Dehydrations with acetic anhydride failed because iron(III) is partly reduced and partly complexed by acetic anhydride or the acetic acid produced upon hydrolysis; reduction was indicated by the presence of iron(II) in the light green crystals remaining after evaporation, and iron(III) complexation by the carbonyl absorption peak present in infrared spectra of the dark iron(III) needles. Although some complexation of the iron(III) by acetic acid or acetic anhydride is indicated, these species do not stabilize iron(III) to any great extent, for the highest reduction potential measured, next to that for the iron(III) perchlorate synthesized by electrolysis, was obtained using selected crystals of the dark iron(III)-rich material.

The azeotropic distillation of iron(III) perchlorate with N,N'-dimethylauramide produced a compound which had a low potential in acetonitrile (+0.6 V vs. the silver reference electrode), indicating the iron(III)-DML complex to be more stable than the iron(III)-acetonitrile complex.

Hydrolysis from trace water contamination was a major problem in the electrolysis experiments. In every case a yellow-orange solution resulted which darkened over a few



hours. Even with special precautions to produce and maintain dry acetonitrile ( $4 \times 10^{-5}\text{M}$  water content) for the measurements and dilutions, hydrolysis was observed in all experiments where the iron(III) concentration was  $2 \times 10^{-3}\text{M}$  or lower. This hydrolysis was evidenced by a decrease in the formal potential of the iron couple and by the presence of an absorption maximum at 359 millimicrons. A maximum at about 350 millimicrons in methanol-water solutions of iron(III) has been assigned to the  $\text{Fe}(\text{OH})^{+2}$  species by Popa, Luca, and Iosif<sup>28</sup>. It is this absorption which tails off into the visible region of the spectrum and accounts for the yellow to red color of hydrated iron(III) perchlorate solutions.

On the basis of these results for the iron(III)-(II) couple it was of interest to look briefly into the difference in  $E_{\frac{1}{2}}$  values observed by Kolthoff and Coetzee for cathodic and anodic scans (see background of PART II or reference 15). If the irreversibility of the couple was due to hydrolysis, the addition of a strong acid such as perchloric acid should make the system more reversible. With precautions to minimize the formation of hydrolyzed iron(III) species in solution by using fresh solutions, by keeping the water concentrations as low as possible, and by adding in some cases small amounts of perchloric acid, plots of  $\log[\text{Fe}(\text{III})/\text{Fe}(\text{II})]$  vs. potential gave straight lines with slopes in the range of 63 to 68



millivolts. Thus the system approaches the reversible value of 59 millivolts as the concentration of iron(III)-hydroxy species is reduced. Indirect evidence from the titration of thiocyanate with hydrated iron(III) in acetonitrile indicates that the principal species is  $\text{Fe}(\text{OH})^{+2}$  (p. 69).

The formal reduction potential of the iron(III)-(II) couple in a solution containing several moles of water per mole of iron and excess perchloric acid was found to be 1.1 V vs. the silver reference electrode.





PART III. IRON(III) AND IRON(II) COMPLEXATION IN ACETONITRILE

BACKGROUND

The stability of complexes in solution is greatly affected by the nature of the solvent. Present theories of nonaqueous coordination chemistry fit available qualitative and semiquantitative data quite well. In most current treatments nonaqueous complexation reactions are considered to be competitions between solvent and ligand for bonding sites on the cation<sup>30</sup>. Thus, the major properties that must be considered are the donor strength of the solvent and of the ligand, and solvent properties such as dielectric constant are neglected. Although this simplification appears to be generally useful in predicting trends, it is still known to be susceptible to variations arising from hydrogen bonding in the solvent, steric hindrance due to large solvent molecules, and polarizability of the solvent, cations, or ligands.

In light of the fact that very few quantitative formation constant measurements have been made on iron(II) complexes, and because anion coordination to iron(II) and iron(III) has a strong effect on the reduction potential of the iron(III)-(II) couple, the formation constants of iron(II) with chloride, bromide, iodide, and thiocyanate were measured and the strength of the



iron(III) complexes of chloride, bromide, and thiocyanate were estimated in acetonitrile. Quantitative data on the formation constants of the iron(II)-anion complexes make it possible to compare observed values with those predicted on a simple complexation basis.



## EXPERIMENTAL

Reagents and Apparatus. The spectrophotometric determinations were performed with a Unicam SP800 ultraviolet-visible spectrophotometer; the spectrophotometer was checked for absorbance accuracy with dichromate-sulfuric acid solution (120 mg potassium dichromate diluted to 1 liter with 0.01M  $\text{H}_2\text{SO}_4$  gives an absorbance of 1.495 @ 235 millimicrons.) The absorbance accuracy was found to be better than  $\pm 0.02$  absorbance units and the reproducibility better than  $\pm 0.005$  absorbance units.

In order to permit mixing of two anhydrous solutions and measurement of the resulting spectra without transfer in and out of a dry box, the apparatus shown in Figure 3 was constructed. A 200-ml volumetric flask was modified for use as a mixing chamber by the addition of a side arm to which a conventional 1-cm rectangular quartz cell was connected by a lapped standard taper joint. The flask stopper was machined from Teflon and had a standard taper on one end and a silicone rubber septum through which the anhydrous solutions were injected on the other end. A 100-microliter Hamilton gas tight syringe with a Teflon tipped plunger, Chaney adapter, and platinum needle was used to make the injections.

All solutions were made up by weight, thermostatted to  $25.0 \pm 0.1^\circ\text{C}$  and the concentrations converted to a molar basis using a density of 778.5 g/l for the experimentally determined density of 0.0100M tetrabutylammonium perchlorate solutions. The cell was thermostatted to  $25.0 \pm 0.1^\circ\text{C}$  inside the



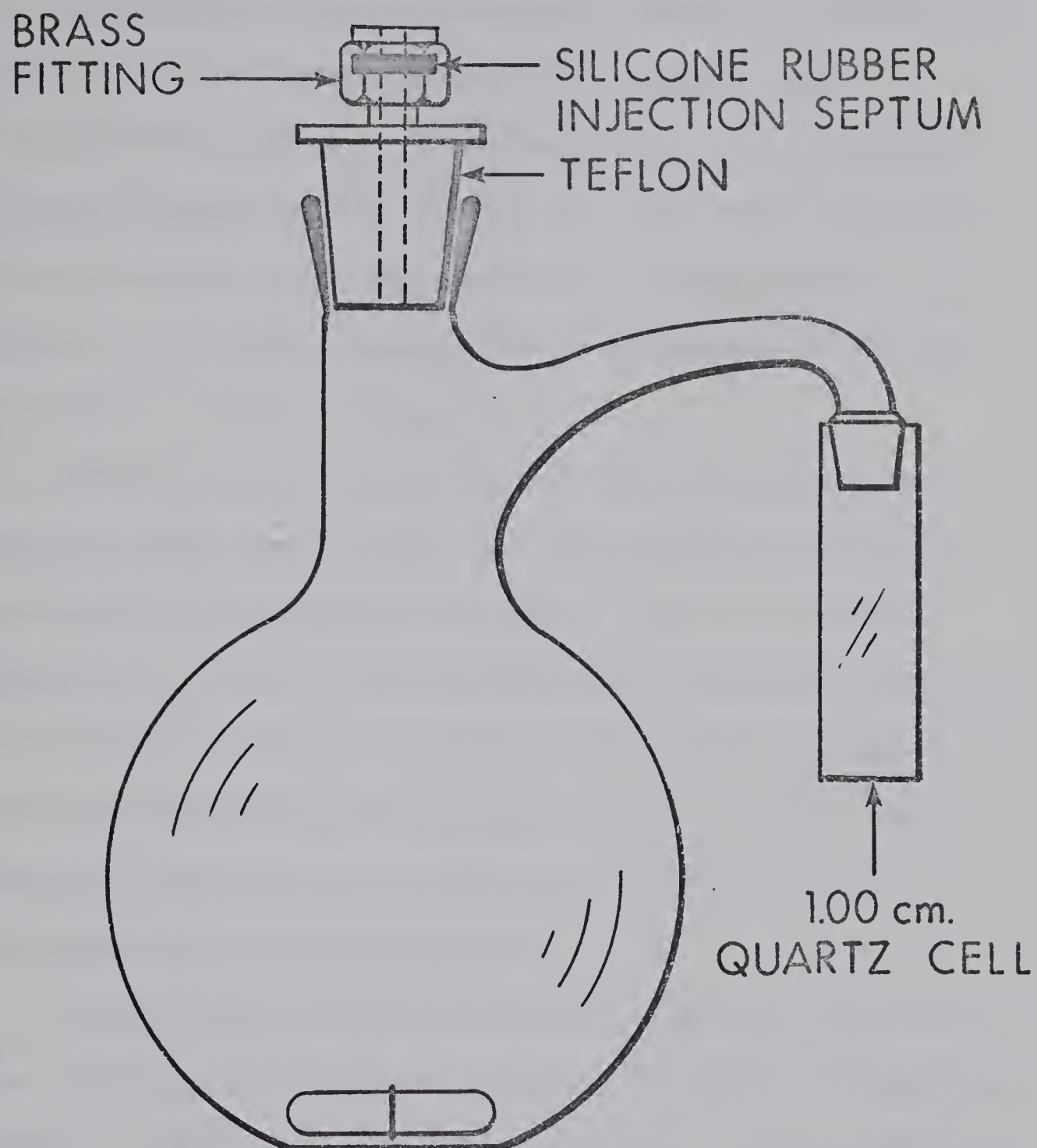


Figure 3. Spectrophotometry cell used in formation constant determinations.





spectrophotometer by means of a water jacketed cell holder and outside the spectrophotometer the mixing chamber was thermostatted by means of a small water bath. The instrument room was thermostatted to  $25.0 \pm 0.3^\circ\text{C}$ . Under these conditions the microliter syringe, equipped with a Chaney adapter, could deliver a calibrated volume to the mixing chamber of the cell to within  $\pm 2$  parts per thousand.

Anhydrous hexakisacetonitrile iron(II) perchlorate was prepared as described in Part II. Acetonitrile was dried and purified by the method given in Part II until it showed no absorption in the ultraviolet down to 225 millimicrons and only 0.1 absorbance at 200 millimicrons. The solvent was deaerated with argon immediately before use to remove traces of oxygen that would otherwise cause oxidation of iodide or iron(II) in the presence of chloride or bromide.

Tetrabutylammonium perchlorate was prepared by precipitation from a boiling aqueous saturated solution of tetrabutylammonium iodide by addition of a saturated solution of sodium perchlorate. Deaeration of the iodide solution was necessary to avoid oxidation to insoluble tetrabutylammonium triiodide (Use of the more expensive bromide salt would avoid this problem). The precipitated perchlorate salt was recrystallized from water until an approximately  $1\text{M}$  solution in acetonitrile did not absorb above 200 millimicrons.



Tetraethylammonium chloride, tetrabutylammonium bromide, and tetrabutylammonium iodide were all recrystallized once, dried in a vacuum over magnesium perchlorate and analyzed by gravimetric silver halide precipitation. The chloride salt due to low solubility in organic solvents was purified by extraction with acetone using a Soxhlet extractor; the product was found to be 99.9% pure. The bromide salt was recrystallized from ethyl acetate. Stirring was necessary to prevent supersaturation; analysis gave a purity of 100.0%. Tetrabutylammonium iodide was recrystallized from a deaerated 10% acetonitrile-water solution and found to be 99.9% pure.

Potassium thiocyanate (Fisher Certified Reagent Grade) was dried for 2 hours at 100°C and found to be 100.1% pure by Volhard titration with silver nitrate.

Method of Formation Constant Measurement. Determinations of the formation constants were made by a mole ratio method. This method involves absorbance measurements of a system in which the concentration of one species is held constant while that of a second is varied. In this work the measurements were made at the wavelength of maximum absorbance of the complex species. The sensitivity of the formation constants to the presence of water required the development of a special procedure for combining and measuring solutions. The experimental procedure consisted first of weighing out into



a Teflon salt cup ( $\frac{1}{4}$  inch high  $\times$   $\frac{1}{4}$  inch I.D.) 5 to 100 mg of hexakisacetonitrile iron(II) perchlorate with a Cahn microbalance in a dry box. The salt cup was placed in the mixing chamber of the cell along with a Teflon stirring bar and a weighed amount (about 90 g) of a freshly deaerated anhydrous solution of 0.0100M tetrabutylammonium perchlorate in purified dry acetonitrile (used to maintain constant ionic strength) was added. The cell was thermostatted, the solution stirred, and the absorbance determined over the required wavelength region. At the same time a concentrated halide solution of accurately known concentration was prepared by weight in a calibrated 25-ml volumetric flask with a Teflon injection top identical to that used in the mixing chamber of the cell. The absorbance of the first complex was then measured at the wavelength of maximum absorbance and plotted as a function of the ligand concentration.

Treatment of Data. A plot of absorbance vs. ligand concentration, obtained by the above method, is shown in Figure 4. The initial region is linear because the ratio of iron(II) to halide is high enough to completely form the 1:1 complex. The molar absorptivity of the first complex is given by the slope of this linear portion of the plot. In the latter part of the curve, where the ratio of iron(II) to halide approaches unity, the plot starts to curve owing to dissociation of the complex. From the molar absorptivity, the concentration



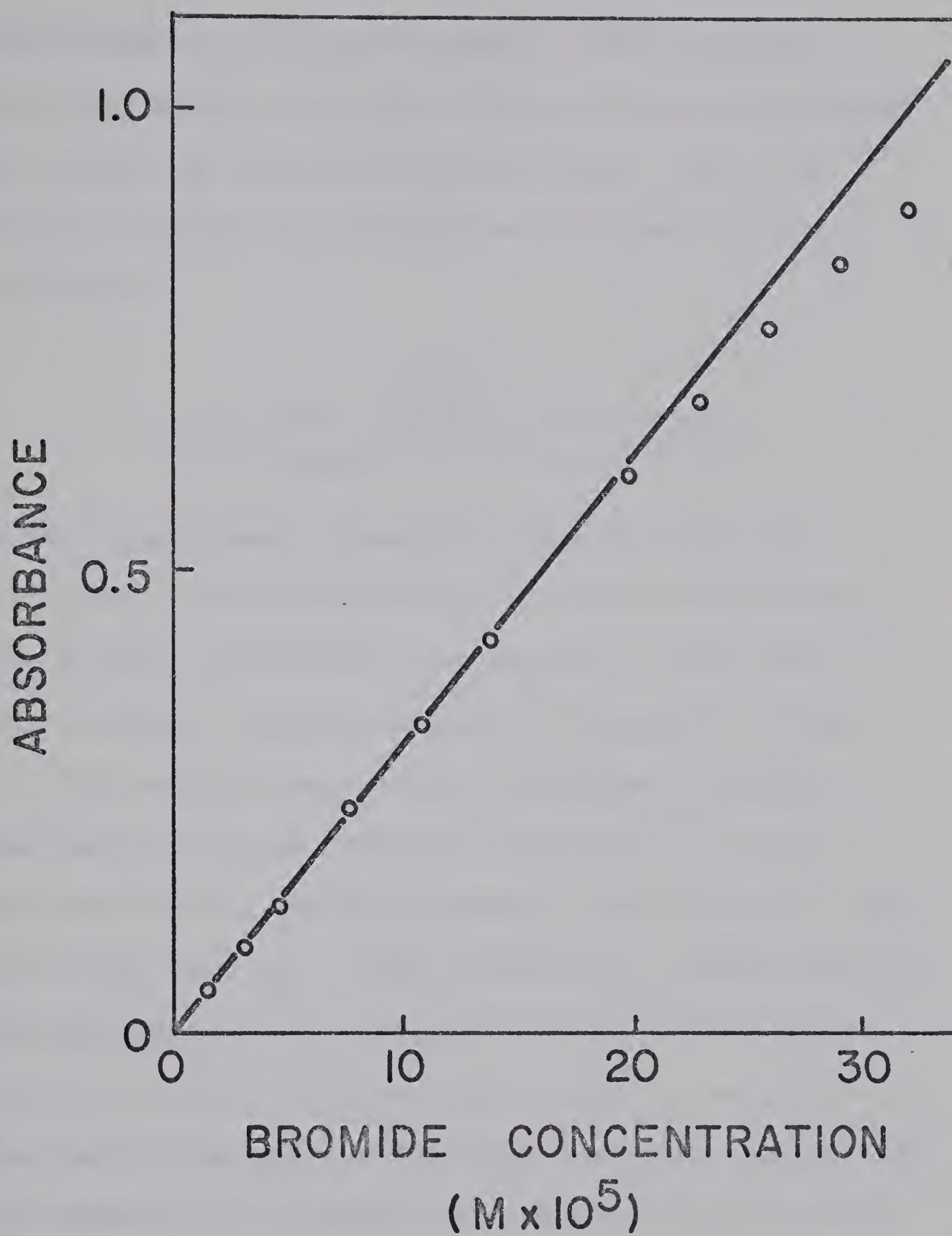


Figure 4. Typical formation constant determination plot [bromide added to iron(II). Data from Trial 4; see Appendix.]





of the complex in the curved region of the plot can be calculated by Beers law; this value is then used to calculate the free halide and iron(II) concentrations. The first formation constant ( $K_1$ ) can then be calculated from the expression:

$$K_1 = \frac{[\text{FeX}^+]}{([\text{Fe(II)}]_{\text{Total}} - [\text{FeX}^+])([\text{X}^-]_{\text{Total}} - [\text{FeX}^+])} \quad (2)$$

In this investigation a computer program was used which calculated all of the concentrations, fit the best straight line to the first portion of the curve by a linear least squares method, and then calculated the formation constant.

This method worked well for the bromide and iodide complexes because the absorption maxima were well enough separated from the absorption maxima of the free iron(II) and halide that there was no need to correct for the absorbance of these species. However, the maximum of the  $\text{FeCl}^+$  complex, which fell at 227 millimicrons, was located on the shoulder of the iron(II) absorption at 205-215 millimicrons. In this case the absorbance of the complex was determined by subtracting the free iron(II) absorbance from the total measured absorbance. The free iron(II) absorbance was calculated by multiplying the molar absorptivity of this species at the wavelength of the  $\text{FeCl}^+$  maximum by the difference between total iron(II) and



total chloride concentrations. Once the absorbance had been corrected for the contribution of iron(II) the data were handled as described for bromide and iodide.

In the case of thiocyanate, where a second complex also formed, the method used was similar to that described above except that the thiocyanate was held at a high constant concentration while the iron(II) concentration was changed by injection of an iron(II) solution. In this case a plot was made of absorbance vs. iron(II) concentration. The plot was similar to those found for the first complex; the molar absorptivity was determined from the initial straight portion, then the curved portion used to obtain values for the formation constant. The second stepwise formation constant is given by the expression:

$$K_2 = \frac{[\text{Fe}(\text{SCN})_2]}{([\text{Fe}(\text{II})_{\text{Total}}] - [\text{Fe}(\text{SCN})_2])([\text{SCN}^-_{\text{Total}}] - [\text{Fe}(\text{SCN})_2] - [\text{Fe}(\text{II})_{\text{Total}}])} \quad (3)$$

Again the data were handled by computer in the same general way as before.



## RESULTS AND DISCUSSION

Results of the formation constant determinations for the iron(II) systems are listed in Table II. The mole ratio method is often used to qualitatively determine the number of ligands in a complex; however, when used with care it is also a satisfactory quantitative technique for the determination of stepwise formation constants less than  $10^8$ . Although the method is tedious, and not as precise as would be desirable, no other common technique could be used on these systems. In an aqueous system many good methods of determining free ligand or free metal concentrations are available for this system; these include the silver, silver halide electrodes as potentiometric indicating electrodes for the halides. However, in acetonitrile free halide concentrations cannot be determined by this method because soluble silver halide anionic complexes form at slow rates<sup>31</sup>. Direct spectrophotometric measurement of uncomplexed halide could not be used because the absorption maxima of the free halide occurred in the region where iron(II) and some of the complexes absorbed. Therefore, the mole ratio method was the only one found applicable.

The Iron(II)-Chloride System. Evidence for only one chloride complex,  $\text{FeCl}^+$ , was found spectrophotometrically



TABLE II. - Summary of Spectrophotometric Data For  
Iron(II)-Anion Complexes

Complex	Log Stepwise Formation Constant	Wavelength of Maximum Absorption of Complex (millimicrons)	Molar Absorptivity at $\lambda_{\text{max}}$
$\text{FeCl}^+$	$5.8 \pm 0.1$	227	$4705 \pm 8$
$\text{FeBr}^+$	$5.5 \pm 0.1$	261	$3148 \pm 26$
$\text{FeI}^+$	$4.3 \pm 0.2$	326	$1553 \pm 294$
$\text{Fe(SCN)}^+$	$5.5 \pm 0.1$	299	$5252 \pm 57$
$\text{Fe(SCN)}_2$	$3.7 \pm 0.1$	289	$10,802 \pm 308$





in acetonitrile. However, the occurrence of further weak complexes with absorption maxima hidden under the free iron(II) or chloride peaks is possible. Spectra recorded at varying ratios of iron(II) to chloride are shown in Figure 5. A problem encountered in this work was oxidation of  $\text{FeCl}^+$  to  $\text{FeCl}_4^-$  by oxygen. With care oxygen could be eliminated; this was shown by the absence of the intense  $\text{FeCl}_4^-$  spectrum when deaeration was used.

From the value of 2.8 for the log formation constant of  $\text{FeCl}^+$  in water<sup>32</sup>, a prediction of the formation constant in acetonitrile was made following the nonaqueous coordination model of Gutmann<sup>30</sup>. Such a prediction requires an a priori estimation of the relative donor strength of acetonitrile and water toward iron(II). According to Gutmann's values of donor numbers for water and acetonitrile, 18.0 and 14.1, respectively, acetonitrile should be the weaker donor of the two. The donor numbers are found by determining the enthalpy of interaction of different solvents with antimony pentachloride<sup>1</sup>. They provide a rough but useful guide if no other information is available concerning specific interaction between a solvent and cation. In the case of iron(II), however, additional data are available in the form of spectrophotometric determinations of the crystal field splitting energy of iron(II) with both acetonitrile and water by Hathaway and Holah<sup>29</sup>. The results



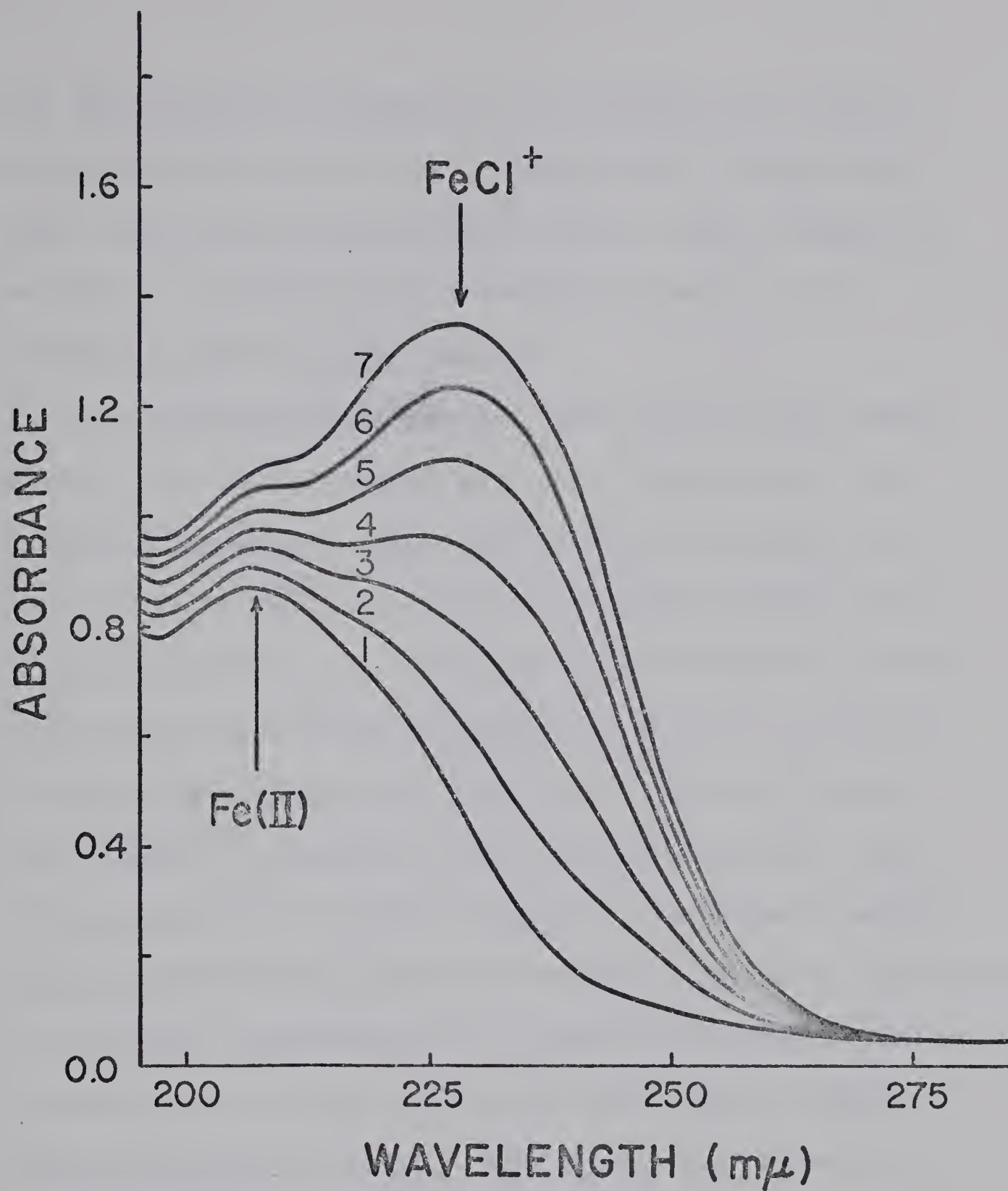


Figure 5. Spectra of iron(II)-chloride complex  
 $[\text{Fe(II)}] = 2.83 \times 10^{-4}\text{M}$ ; ratio of  $[\text{Cl}^-]$  to  $[\text{Fe(II)}] =$   
0, 0.17, 0.33, 0.50, 0.66, 0.83, 0.99 for curves 1 to 7.



show that there is a slight specific interaction of iron(II) with acetonitrile which gives it greater donor strength than water. Applying this experimental relative donor strength to the theory of Gutmann gives for the  $\text{FeCl}^+$  complex a log formation constant of less than 2.8.

This estimated value does not agree with the experimental value of 5.8. The difference may result from the fact that the simple coordination model does not take into account the effect of the difference in dielectric constant between water, 81, and acetonitrile, 36. A solvent of low dielectric constant cannot stabilize a highly charged cation as well as a solvent of high dielectric constant; therefore, a cation will have a higher energy in a solvent of low dielectric constant. When cations coordinate to neutral ligands no significant change in charge separation takes place and the energy gained by complexation will be nearly independent of the dielectric constant. However, the effect may be entirely different when a highly charged cation coordinates to anions. Here partial neutralization of the positive charge occurs and complexation should therefore be quite dependent on the dielectric constant of the solvent and the charge on the cation. The above rationale explains qualitatively why stronger complexation may be seen even in the presence of stronger interaction between cation and solvent.



Iron(II)-Bromide System. Only one bromide complex,  $\text{FeBr}^+$ , was observed spectrophotometrically in acetonitrile, even at high bromide to iron(II) ratios (Figure 6). In this case the absorption of a higher order complex should fall in a wavelength region of the ultraviolet not obscured by the free bromide and iron(II) spectra, and so should be readily seen. Here, as in the case of the chloride system, trace oxygen causes oxidation to the stable  $\text{FeBr}_4^-$  species, which could be identified by its distinctive intense spectrum, in the same way as  $\text{FeCl}_4^-$  was.

Although values of the formation constant for  $\text{FeBr}^+$  in water are not available for comparison, the log formation constant of 5.5 found in acetonitrile correlates with the accepted donor strength of bromide compared to chloride. In most cases the donor strength of bromide is less than chloride, so the corresponding complexes are weaker.

Iron(II)-Iodide System. Only one iodide complex,  $\text{FeI}^+$ , was found in acetonitrile (Figure 7). The formation constant of the iodide complex was determined from both directions, that is, from measurements taken by adding iodide to iron(II) and vice versa. As the results obtained by both methods were identical, the absence of higher iodide complexes or polynuclear species seems certain. In this system traces of oxygen caused relatively large experimental deviations, not because the iron(II)-iodide complex was oxidized, but because iodide





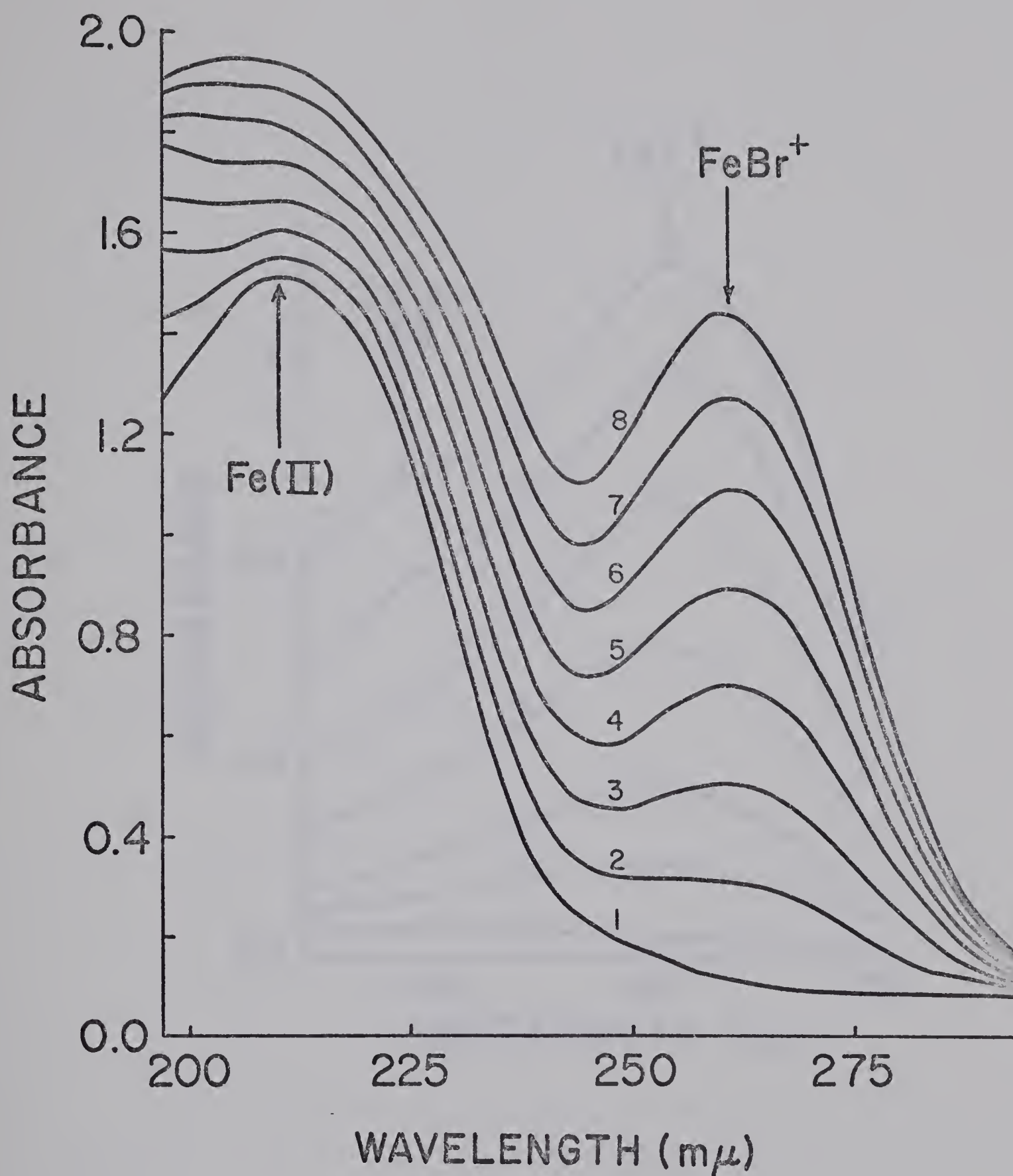


Figure 6. Spectra of iron(II)-bromide complex  
[Fe(II)] =  $6.03 \times 10^{-4}M$ ; ratio of  $[Br^-]$  to  $[Fe(II)]$  =  
0, 0.10, 0.21, 0.31, 0.42, 0.52, 0.62, 0.73 for curves  
1 to 8.



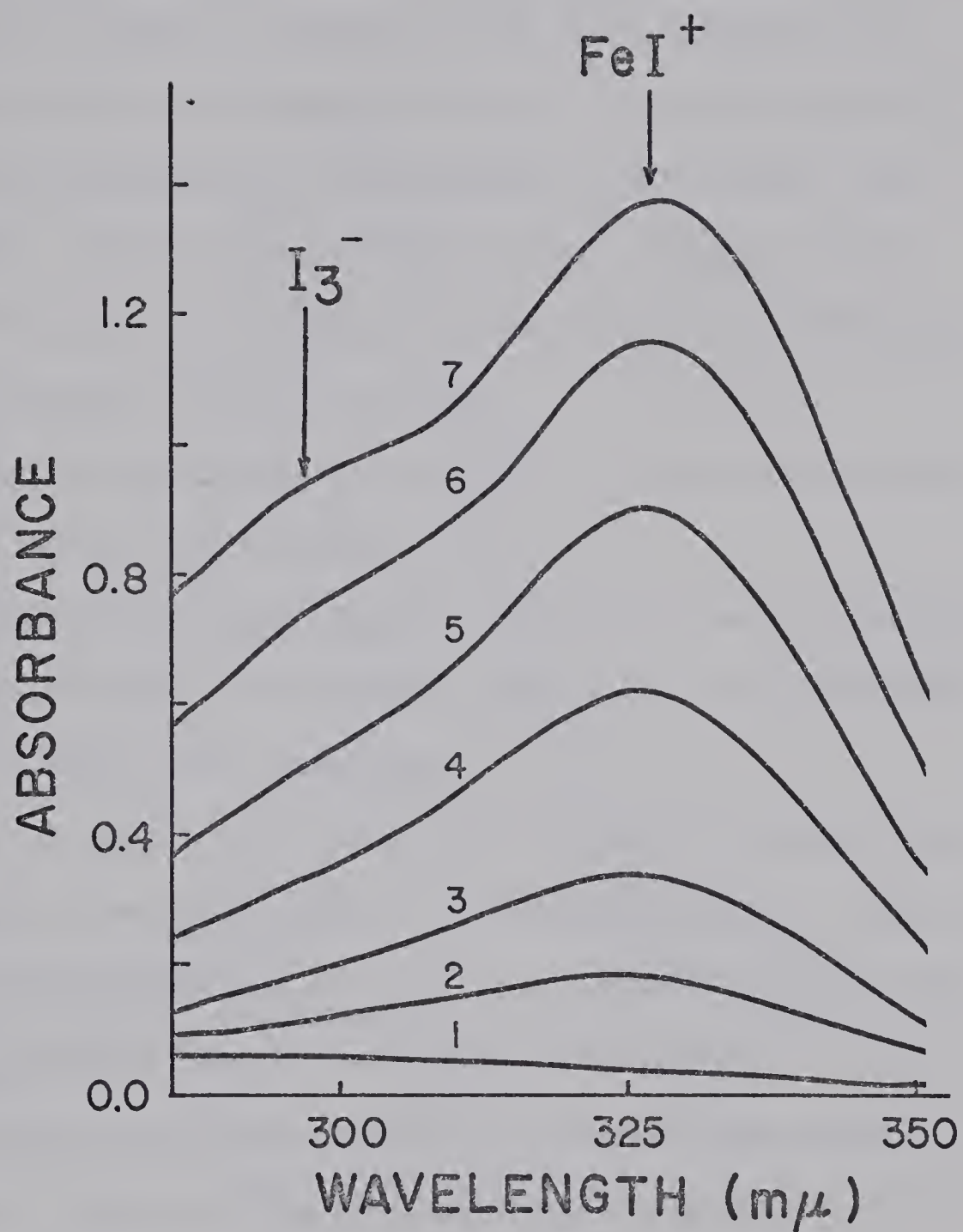


Figure 7. Spectra of iron(II)-iodide complex  
[Fe(II)] =  $1.25 \times 10^{-3}M$ ; ratio of  $[I^-]$  to  $[Fe(II)]$  =  
0, 0.09, 0.19, 0.38, 0.56, 0.75, 0.91 for curves 1 to 7.



itself oxidized directly to the highly stable triiodide ion, which has a formation constant of  $10^{7.40}$ .<sup>33</sup> Diffusion of oxygen into the spectrophotometric cell over the course of a set of spectrophotometric measurements, about 4 hours, was detectible. With care to minimize oxygen diffusion and by doing the experiment as rapidly as possible, this interference could be reduced but not eliminated.

Again the log formation constant, 4.3, fits the predicted trend in halide donating power.

Iron(II)-Thiocyanate System. In this system two complexes were found,  $\text{Fe}(\text{SCN})^+$  and  $\text{Fe}(\text{SCN})_2$  (Figure 8). No evidence was found for higher order complexes.

The log of the first thiocyanate formation constant, 5.5, is slightly lower than that of the chloride complex. Early work on thiocyanate complexes of iron(II) in water<sup>34</sup> indicates that they are formed either only slightly or not at all.

A second thiocyanate complex is observed spectrophotometrically, and has a log stepwise formation constant of 3.7.

A check for formation of polynuclear complexes involving more than one iron(II) was made by repeating the mole-ratio measurements over iron(II) concentrations from  $0.50 \times 10^{-3}\text{M}$  to  $2.15 \times 10^{-3}\text{M}$ . The fact that the molar absorptivity remained constant indicated no polynuclear species were present.





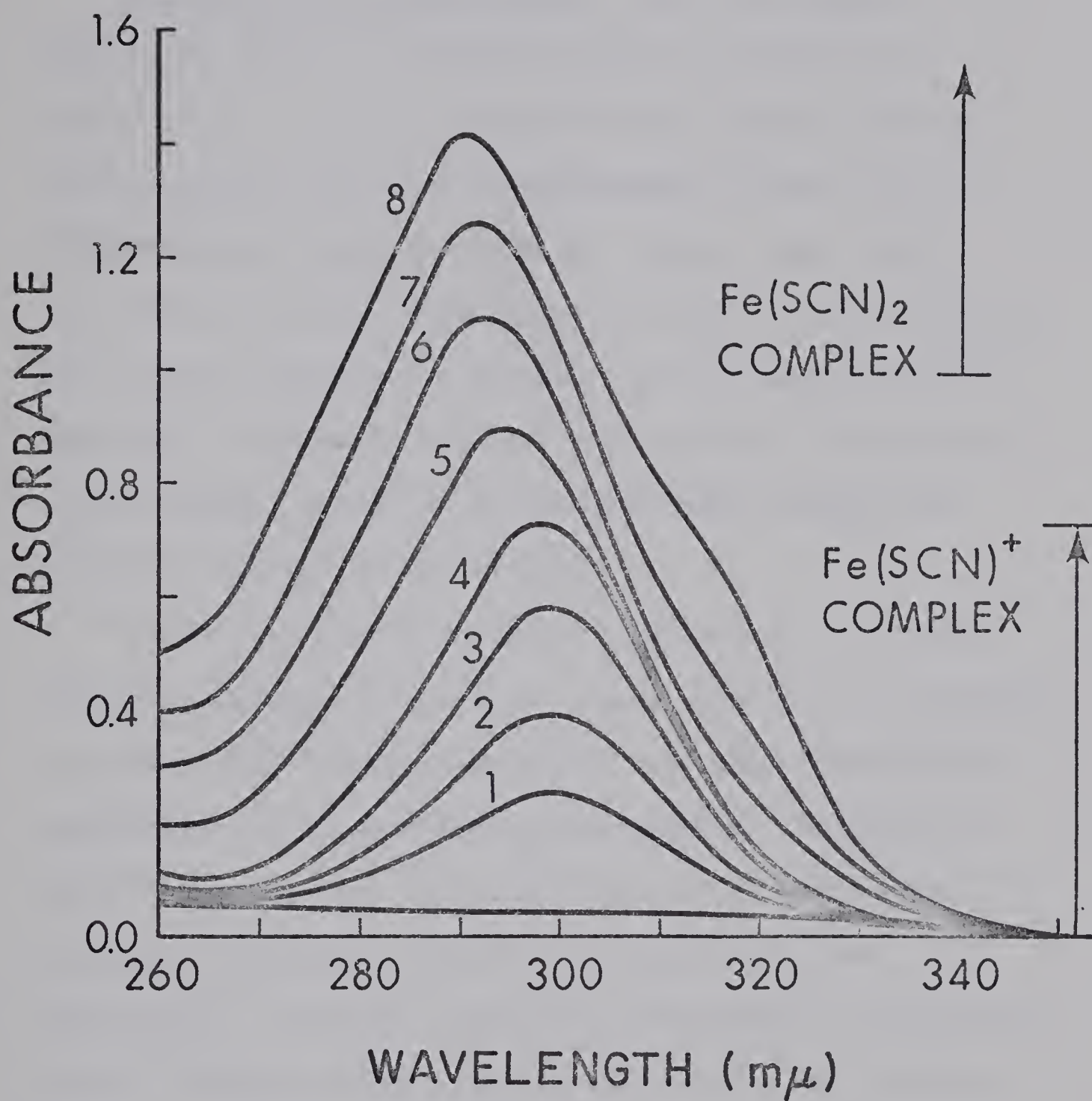


Figure 8. Spectra of iron(II)-thiocyanate complexes  
[Fe(II)] =  $1.53 \times 10^{-4}\text{M}$ ; ratio of [SCN<sup>-</sup>] to [Fe(II)] =  
0.27, 0.45, 0.72, 1.00, 1.54, 2.22, 2.86, and 4.00 for  
curves 1 to 8.





The Iron(III)-Chloride System. Due to the highly hygroscopic nature of anhydrous iron(III) solutions in acetonitrile, and to the formation of very stable iron(III)-hydroxy species, quantitative measurements of the iron(III) halide complexes could not be made. However, some idea of the extent of anionic complexation of iron(III) can be inferred from indirect experimental evidence. The formation of stable complexes is favored by the fact that iron(III) is a hard acid of high charge, as well as by both the donor strength and dielectric constant of the solvent.

The iron(III)-chloride system in acetonitrile has been studied by Gutmann and Lux<sup>35</sup>, who found three strong tetrahedral complexes,  $\text{FeCl}^{+2}$ ,  $\text{FeCl}_3$ , and  $\text{FeCl}_4^-$  from spectrophotometric, potentiometric, and conductance measurements. Hathaway and Holah<sup>29</sup> reported that  $\text{FeCl}_3$  when dissolved in acetonitrile undergoes a solvolysis reaction to produce  $\text{FeCl}_4^-$  and  $\text{Fe}(\text{CH}_3\text{CN})_6^{+3}$ . To obtain a qualitative estimate of the relative overall affinity of the iron(III) and iron(II) for chloride, the potential of a 1 to 1 mixture of iron(II) perchlorate and hydrated iron(III) perchlorate at a concentration of 0.01M in each was measured both before and after the addition of chloride. If iron(III) is more strongly complexed than iron(II), the potential of the couple should decrease. It was found that the potential decreased by 0.06 V in 0.01M chloride and 0.24 V in



0.05M chloride. Thus the overall formation constant for iron(III) with chloride is greater than it is for iron (II). It is impossible, however, to make an accurate estimate of the strengths because of the interference caused by iron(III) hydrolysis.

The Iron(III)-Bromide System. Bromide complexes with iron(III) in acetonitrile have not been studied. Potential measurements made on solutions 0.01M in both iron(II) and iron(III) perchlorate gave a potential decrease of 0.07 V in the presence of 0.01M bromide and 0.28 V with 0.05M bromide. Thus overall complexation of iron(III) by bromide is greater than that of iron(II).

The Iron(III)-Thiocyanate System. Thiocyanate complexation by iron(III) is responsible for the interesting thiocyanate titration described in the next section. It is postulated that in solutions of hydrated iron(III) perchlorate,  $\text{Fe(III)}$  and  $\text{FeOH}^{+2}$  coordinate with thiocyanate to form stable  $\text{Fe(SCN)}_6^{-3}$  and  $\text{Fe(SCN)}_5\text{OH}^{-3}$  species. A coordination number of six is predicted because thiocyanate is known to form complexes of high coordination number. Under the experimental conditions used it is estimated that a portion of the iron(III) is present as  $\text{FeOH}^{+2}$  in hydrated iron(III) perchlorate solutions. Thiocyanate probably is not strong enough to displace hydroxy species already attached to the iron(III). Evidence for a



thiocyanate coordination number of about six is given in the next section. Lower iron(III)-thiocyanate complexes may be formed, but apparently do not stabilize iron(III) enough to prevent oxidation of thiocyanate to thiocyanogen.



PART IV. HYDRATED IRON(III) PERCHLORATE AS AN ANALYTICAL OXIDANT

BACKGROUND

As in acid-base titrimetry, the applications of oxidation-reduction titrations may be extended by use of a solvent other than water. Nonaqueous solvents can alleviate problems of insolubility of organic compounds or reaction intermediates such as free radicals, and reactions (decomposition through hydrolysis, etc.) of products or intermediates with water. For this reason nonaqueous redox titrimetry may become a useful analytical method. Information in this area is limited and much further study is needed.

Previous work in this area was done mostly in glacial acetic acid as a solvent, using as titrants lead(IV) acetate, cerium(IV), permanganate, bromine and several other compounds<sup>4-6</sup>. Reactions in this medium of low dielectric constant ( $\epsilon=6.4$ ) generally are slow and equivalence points uncertain. Addition of acids or bases such as sodium acetate or perchloric acid often increases reaction rates, apparently by helping in the formation of ionic species which facilitate electron transfer.

A far more suitable solvent for oxidation-reduction titrations is acetonitrile. It has a moderate dielectric constant of 36, good stability to both oxidation and reduction, a polarographic range of +2.3 to -2.7 V vs. the silver, 0.1M





silver nitrate in acetonitrile reference electrode<sup>11</sup> and little acid or base character. The autoprotolysis constant is  $1 \times 10^{-39}$ .<sup>12</sup> Rao and Murthy have studied ammonium hexanitratocerate<sup>16-18</sup> as an oxidant and found it to be reasonably satisfactory in the presence of acetic acid.

Recently copper(II) perchlorate in acetonitrile has been found to be a stable oxidant<sup>20-23</sup>. It quantitatively oxidizes a number of compounds, including iodide, hydroquinone, aryl amines, thioureas, and ferrocenes. The only drawback to its use is that the standard reduction potential, +0.800 V vs. the silver reference electrode for anhydrous copper(II) perchlorate, is not high enough in many cases. For this reason a study has been undertaken of the use of hydrated iron(III) perchlorate as a redox titrant. As mentioned previously, the iron(III) reduction potential of about +1.1 V vs. the silver reference electrode makes it 0.3 V more powerful than anhydrous copper(II) perchlorate.



## EXPERIMENTAL

Reagents. Acetonitrile was purified as described previously in PART II. Commercial hydrated iron(III) perchlorate was used as received.

All compounds studied in this work, with the exception of the phenothiazines, N,N'-diphenyl-p-phenylenediamine (DPPD), potassium iodide, and tetrachlorohydroquinone, were recrystallized once from acetonitrile. Phenothiazine and tetrachlorohydroquinone were vacuum sublimed. The phenothiazine drugs were converted from the hydrochloride or carboxylate salts to the corresponding perchlorates by precipitation from aqueous solution through addition of a concentrated solution of sodium perchlorate, followed by filtration and drying under a vacuum. This conversion was necessary in order to provide adequate solubility in acetonitrile and to avoid the presence of anions which would lower the potential of iron(III) by complexation. DPPD was recrystallized 4 times from benzene using Norite A decolorizing charcoal. Potassium iodide was purified by several recrystallizations from water containing a slight amount of hydriodic acid, then dried in a high vacuum at 200°C.

Potentiometric Titrations. Most of the potentiometric titrations were run under nitrogen in the Teflon-stoppered



titration vessel shown in Figure 9. Titrant delivery and potential recording were done with a Metrohm Model 436E automatic titrator. Titration times ranged from 20 to 200 minutes, depending on the reaction rate of the system under study.



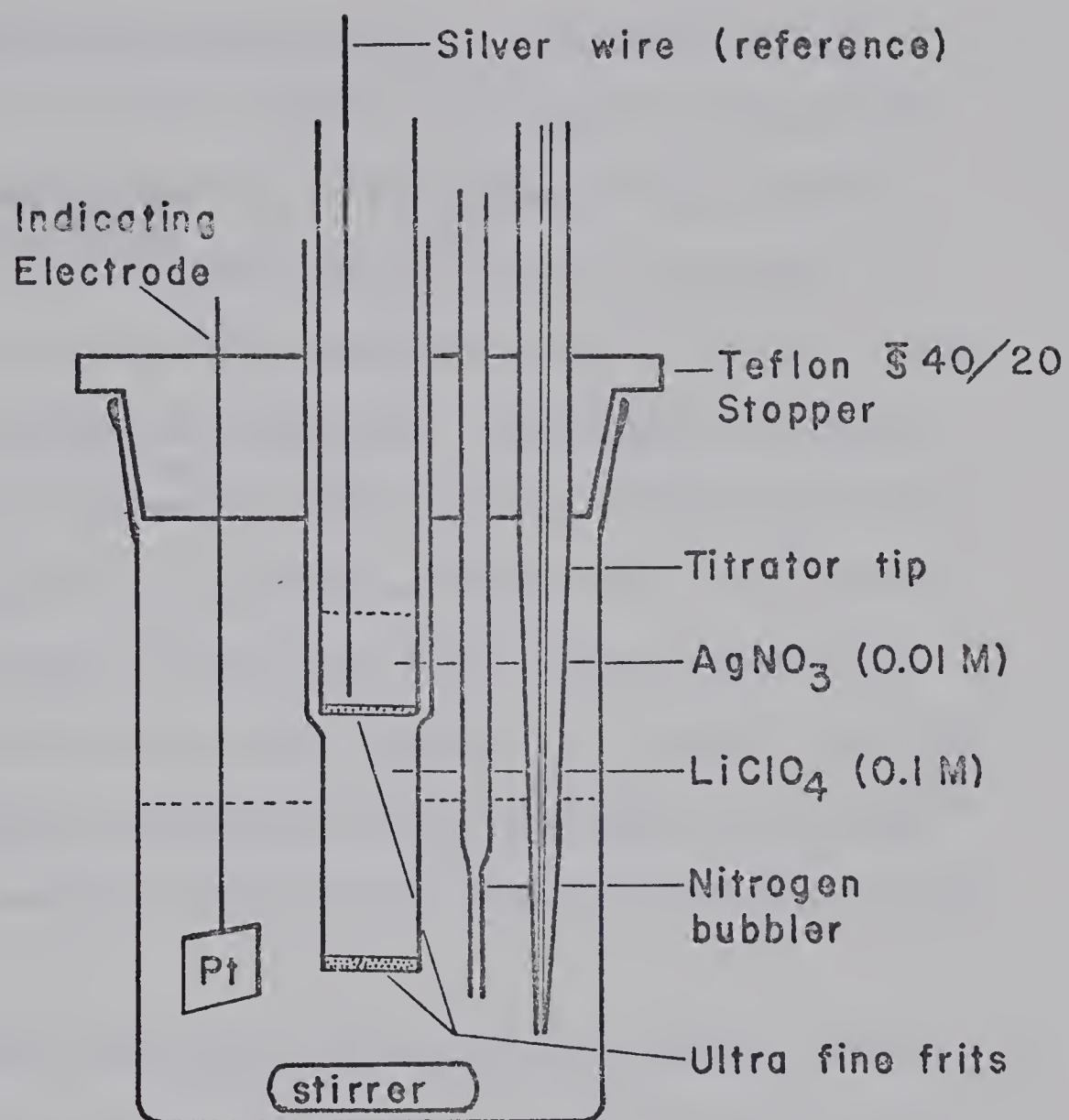


Figure 9. Potentiometric titration cell





## RESULTS AND DISCUSSION

Standardization and Stability. Approximately 0.1M solutions of iron(III) titrant were prepared from hydrated iron(III) perchlorate (G. F. Smith Chemical Co., Columbus, Ohio, and Alfa Inorganics, Beverly, Mass.) and stored in a reservoir protected from atmospheric water with drying tubes containing magnesium perchlorate. The commercial iron(III) perchlorate contained at least six moles of water per mole of iron, in addition to hydrated perchloric acid. The material as received was a sticky mass of pale violet crystals and standard solutions could not be prepared by weight. Solutions of approximate concentration could be prepared by assuming that the commercial material contained about 65%  $\text{Fe}(\text{ClO}_4)_3$  by weight.

Accurate determination of the concentration of iron(III) in the titrant solutions was difficult. Total iron(III) could be determined by titration with a standard solution of EDTA; however, not all of the iron(III) titrated by EDTA is available for oxidation because some of it is present as an iron(III)-hydroxy species. Complexation of iron(III) by hydroxide lowers the reduction potential so much that iron(III) cannot function effectively as an oxidant. Therefore standardization by an oxidation-reduction titration is necessary. Titrations of



potassium iodide, tetrachlorohydroquinone, and ferrocene showed, however, that this method of standardization gave variations for the same solution on the order of  $\pm 2\%$ . Greater accuracy could not be obtained because the iron(III)-hydroxy species though capable of oxidizing compounds of low reduction potential, cannot more stable ones. Thus the molarity is a function of the reduction potential of the compound titrated. The best way to standardize this titrant then is with a pure sample of the compound to be determined or with a standard compound which has a similar reduction potential.

Iron(III) solutions were prepared from several grades of acetonitrile, ranging from commercial technical (containing about 0.2%  $\text{H}_2\text{O}$ ) and dried technical grade to dry, purified material. With respect to stability and convenience the dry technical grade solvent, prepared by refluxing technical grade acetonitrile with calcium hydride, was preferred. The presence of water in the solvent and in the iron(III) perchlorate salt causes slow hydrolysis that results in drawn out end point inflections and decreasing molarities. This problem can be avoided by preparing fresh solutions daily. Removal of other impurities did not seem to be critical.

In order to test the stability of the titrant, several solutions were made up in acetonitrile of varying purity levels and standardized daily for two weeks against potassium iodide.



The molarities decreased about 1% a day when as-received technical grade acetonitrile was used, and about 0.1% a day when dried technical grade acetonitrile was used. From these results it can be seen that dried acetonitrile is a more satisfactory solvent, and also that for accurate results daily standardization is necessary.

The decrease in molarity on standing is caused by hydrolysis and not reduction since addition of 70% perchloric acid increases the molarity. Attempts to use perchloric acid to stabilize the titrant by adding 1 to 5 ml 70% perchloric acid failed because the extra water in 70% perchloric acid more than offset the benefit of the additional acid. Other attempts to remove some of the water by adding 5 to 10 ml of acetic anhydride to the titrant also failed because the anhydride or the resulting acetic acid caused reduction of a portion of the iron(III).

Scope and mechanisms of reactions investigated. To assess the scope of oxidation by iron(III) in acetonitrile a number of organic compounds were titrated. Table III lists those investigated that showed well defined titration breaks. Several of these reactions will be discussed in some detail, but in general, compounds oxidized by copper(II) are also oxidized by iron(III), as well as many more for which copper is too weak. Thus, while carbazole is not attacked by



TABLE III. - Compounds Titrated with Hydrated Iron(III) Perchlorate in Acetonitrile  
(in alphabetical order)

Compound	Structure	Potential Break, mV*	Stoichiometry	Relative Reaction Rate**
Benzidine		150	2	fast
Carbazole		170	2	slow
Dimethoxybenzidine		100, 100	0.5, 2	fast
Diphenylbenzidine		50, 350	0.5, 2	very fast
Diphenylguanidine		900	0.25	moderately fast
N,N'-Diphenyl-p-phenylenediamine		120, 250	1.0, 2.0	very fast

\* Defined as difference in potential at 90% and 110% of end point.

\*\* Time required for potential stabilization (fast, about ½ minute; slow, over 4 minutes).





TABLE III. - Continued

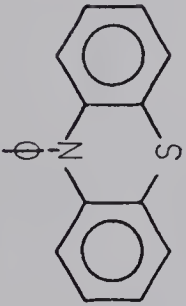
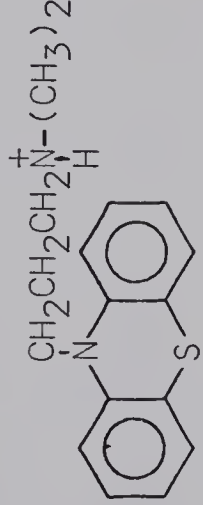
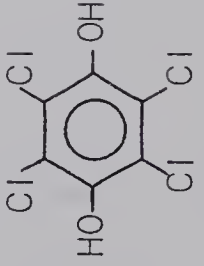
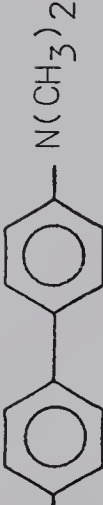
Compound	Structure	Potential Break, mV*	Stoichiometry	Relative Reaction Rate**
Ferrocene	<chem>(C5H5)2Fe</chem>	700	1.00	very fast
Hydroquinone	<chem>Oc1ccc(O)cc1</chem>	400	2.0	moderately fast
2-Mercaptobenzothiazole	<chem>S=C1Nc2ccccc2S1</chem>	600	1	very slow
2-Naphthalenethiol	<chem>S=C1Nc2ccccc2S1</chem>	550	1	moderately fast
Phenothiazine	<chem>c1ccc2c(c1)nc3ccccc3s2</chem>	150, 175	1.0, 2.0	fast
N-Phenylcarbazole	<chem>c1ccc2c(c1)nc3ccccc3n2</chem>	50	2	slow

\* Defined as difference in potential at 90% and 110% of end point.

\*\* Time required for potential stabilization (fast, about ½ minute; slow, over 4 minutes).



TABLE III. - Continued

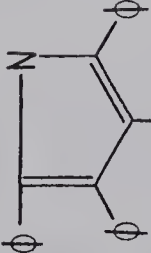
Compound	Structure	Potential Break, mV*	Stoichiometry	Relative Reaction Rate**
N-Phenylphenothiazine		300, 50	1.0, 2.5	fast
Potassium Iodide	KI	300, 500	0.66, 1.00	moderately fast
Potassium Thiocyanate	KSCN	300, 300	0.19, 1.00	fairly slow
Promazine Perchlorate		150, 100	1.0, 2.1	very slow
Tetrachlorohydroquinone		250	2.0	fairly slow
Tetramethylbenzidine		250	2	moderately fast

\* Defined as difference in potential at 90% and 110% of end point.

\*\* Time required for potential stabilization (fast, about ½ minute; slow, over 4 minutes).



TABLE III. - Continued

Compound	Structure	Potential break, mV*	Stoichiometry	Relative Reaction Rate**
Tetramethylthiourea	$(\text{CH}_3)_2\text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{N}(\text{CH}_3)_2$	700	1.0	moderately fast
Tetraphenylpyrrole		200	2	fairly slow
Thioacetamide	$\text{CH}_3 - \overset{\text{S}}{\parallel} \text{C} - \text{NH}_2$	600	1	moderately fast
Thioacetanilide	$\text{CH}_3 - \overset{\text{S}}{\parallel} \text{C} - \text{N}(\text{H}) - \phi$	120	2	moderately fast
Thiocarbanilide	$\text{H}_2\text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{N}(\text{H}) - \phi$	600	1	fairly slow
Thiourea	$\text{H}_2\text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{NH}_2$	500	1	fast

\* Defined as difference in potential at 90% and 110% of end point.

\*\* Time required for potential stabilization (fast, about ½ minute; slow, over 4 minutes).



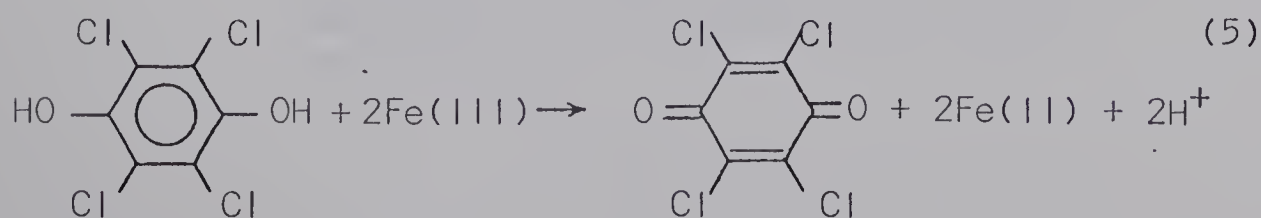
copper(II), it shows a well defined stoichiometric reaction with iron(III) (Figure 10a).

Those ferrocenes which react stoichiometrically with copper(II)<sup>23</sup> can also be titrated with hydrated iron(III).



Ferrocene itself gives a sharp break of 700 mV at the end point (Figure 10b). A small amount of water, on the order of 0.1M, in the ferrocene solution is sometimes necessary to prevent further oxidation of the ferricinium ion. Under these conditions ferrocene is a convenient standard of low reduction potential for iron(III). It has been shown to be a satisfactory primary standard for copper(II) to better than a part per thousand<sup>23</sup>.

Hydroquinone, which is also titrated by copper(II) perchlorate<sup>20</sup>, is readily oxidized by iron(III). It could be used as a standard for iron(III) if it did not show a tendency to air oxidize during storage. Tetrachlorohydroquinone (Figure 11a) is not susceptible to air oxidation, and gives a small but stoichiometric two electron break. It may be useful as a standard in iron(III) where a compound of high reduction potential is to be determined. The reaction is







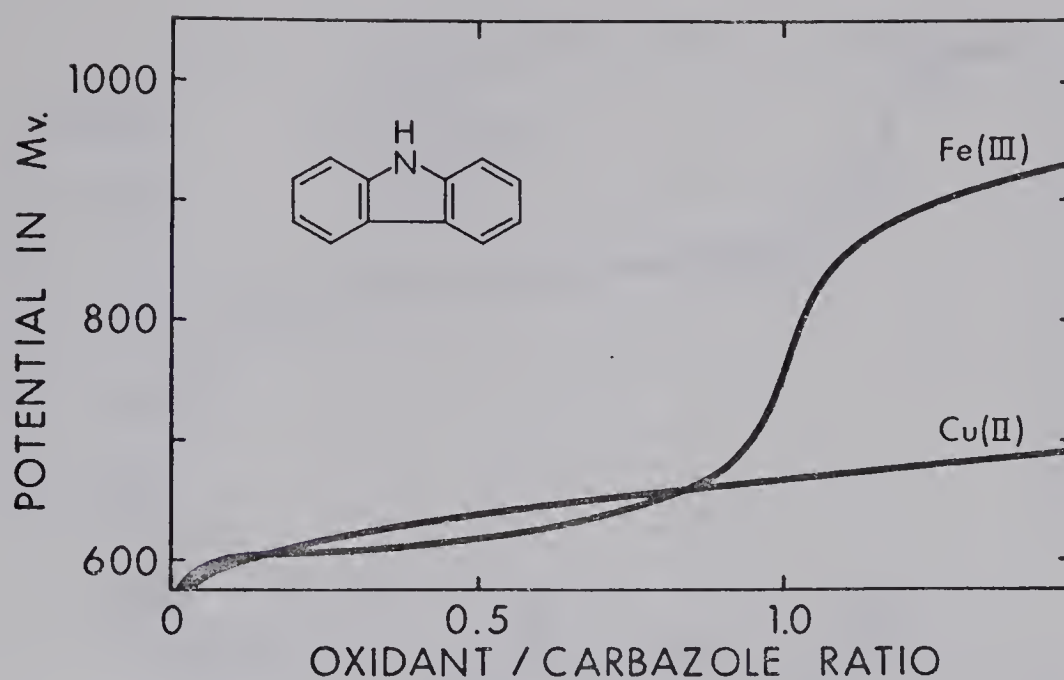


Figure 10a. Potentiometric titration of carbazole with 0.1M copper (II) perchlorate and 0.1M hydrated iron(III) perchlorate

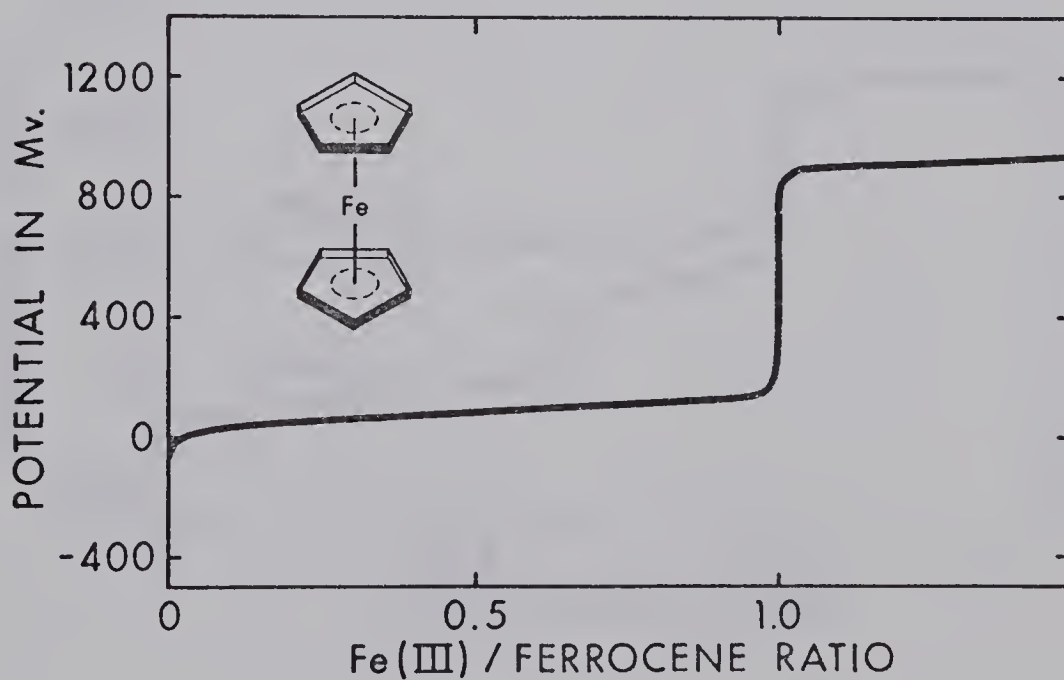


Figure 10b. Potentiometric titration of ferrocene with 0.1M hydrated iron(III) perchlorate



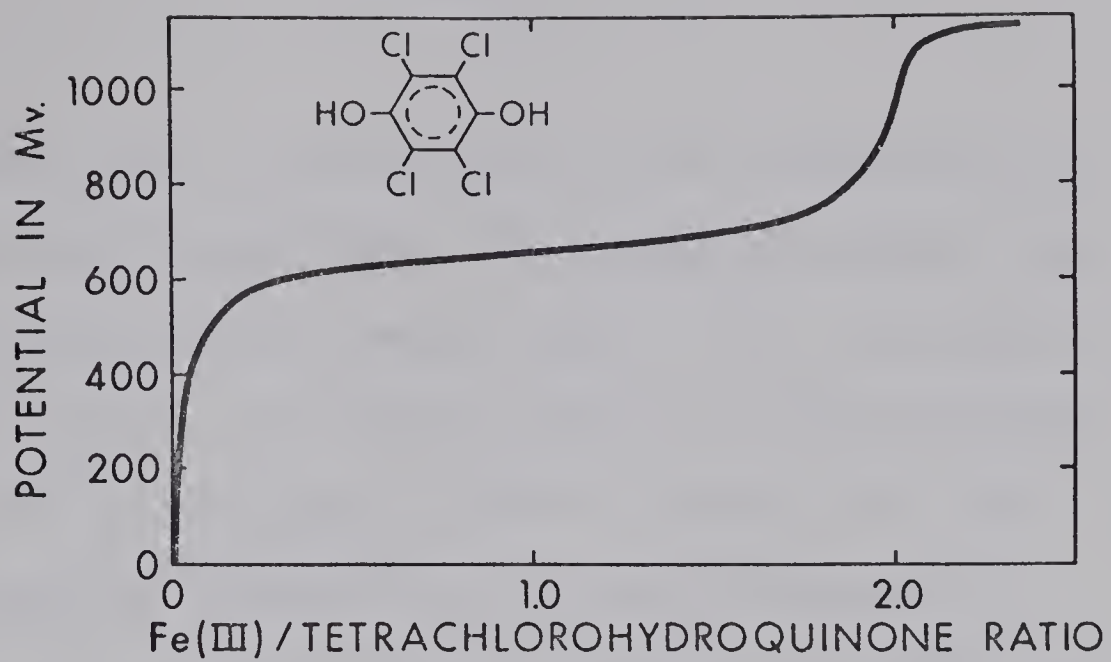


Figure 11a. Potentiometric titration of tetrachlorohydroquinone with 0.1M hydrated iron(III) perchlorate

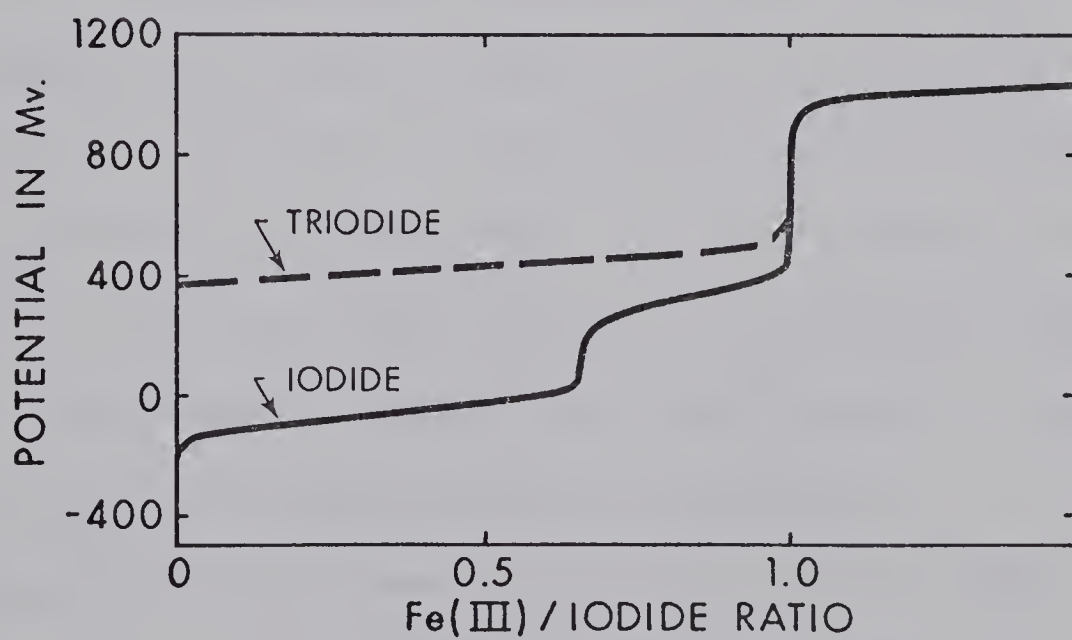
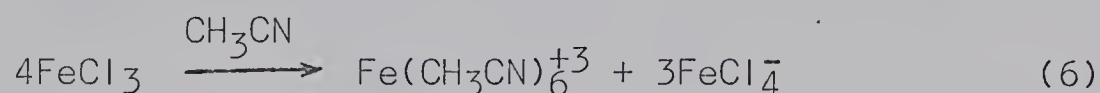


Figure 11b. Potentiometric titration of iodide and triiodide with 0.1M hydrated iron(III) perchlorate



Another class of compounds which were investigated were the halides and pseudohalides. These compounds present some of the most interesting chemistry found in this investigation. Fluoride, chloride, and bromide, because of high electronegativities, are not oxidized by iron(III); however, all form strong complexes. Chloride is so strongly tetrahedrally coordinated to the iron(III) that Hathaway and Holah<sup>29</sup> found that anhydrous iron(III) chloride when dissolved in acetonitrile underwent solvolysis according to the equilibrium:



Iodide, on the other hand, does not form an iron(III)-iodide complex, but instead is oxidized first to triiodide, then to iodine (Figure 11b). The triiodide ion has a sufficiently large formation constant that a distinct potential break is seen<sup>33</sup>. Potassium iodide, available in high purity upon drying of the commercial reagent grade salt<sup>26</sup>, could find some use as a standard of moderate reduction potential.

Thiocyanate lies between iodide and the other halides with respect to ease of oxidation, and for this reason exhibits both complexing and oxidizing behavior. Titrations with iron(III) show two well defined breaks at iron(III) to thiocyanate ratios of 0.19 and 1.00 (Figure 12).

The first inflection is attributed to the



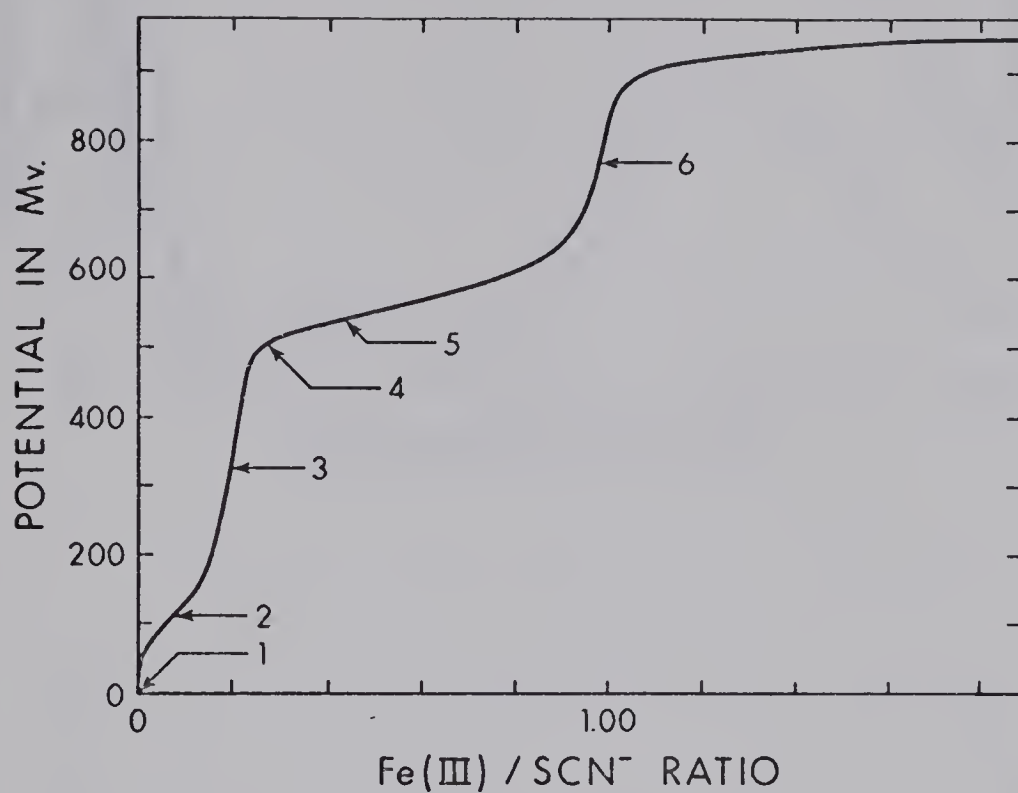


Figure 12. Potentiometric titration of potassium thiocyanate with 0.1M hydrated iron(III) perchlorate (Arrows indicate points at which spectra were taken. See Figure 13)





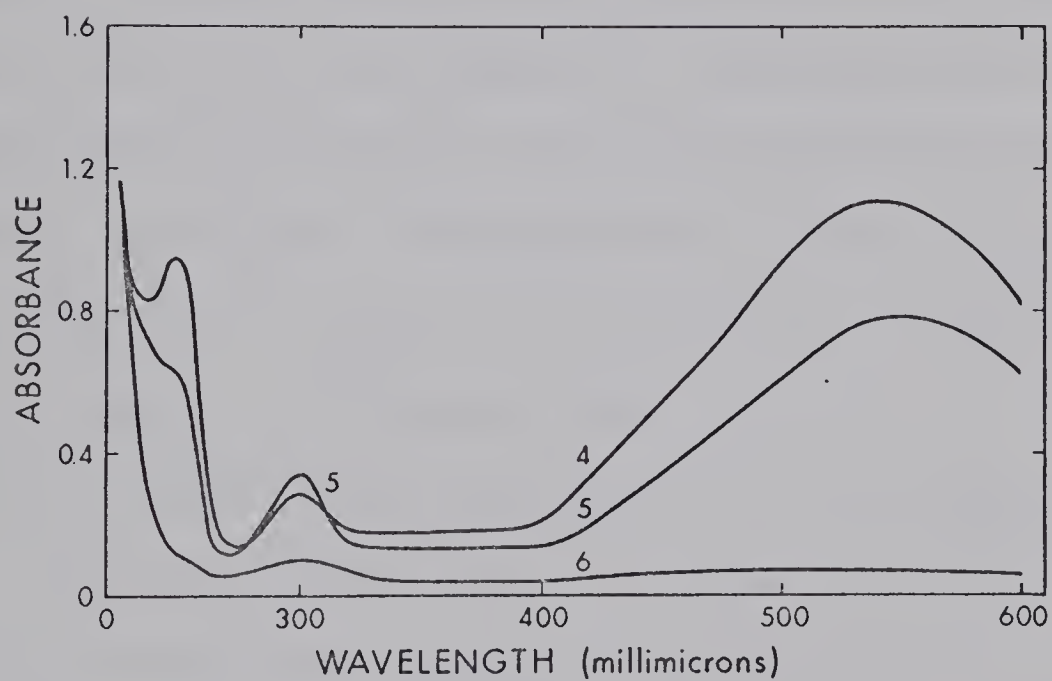
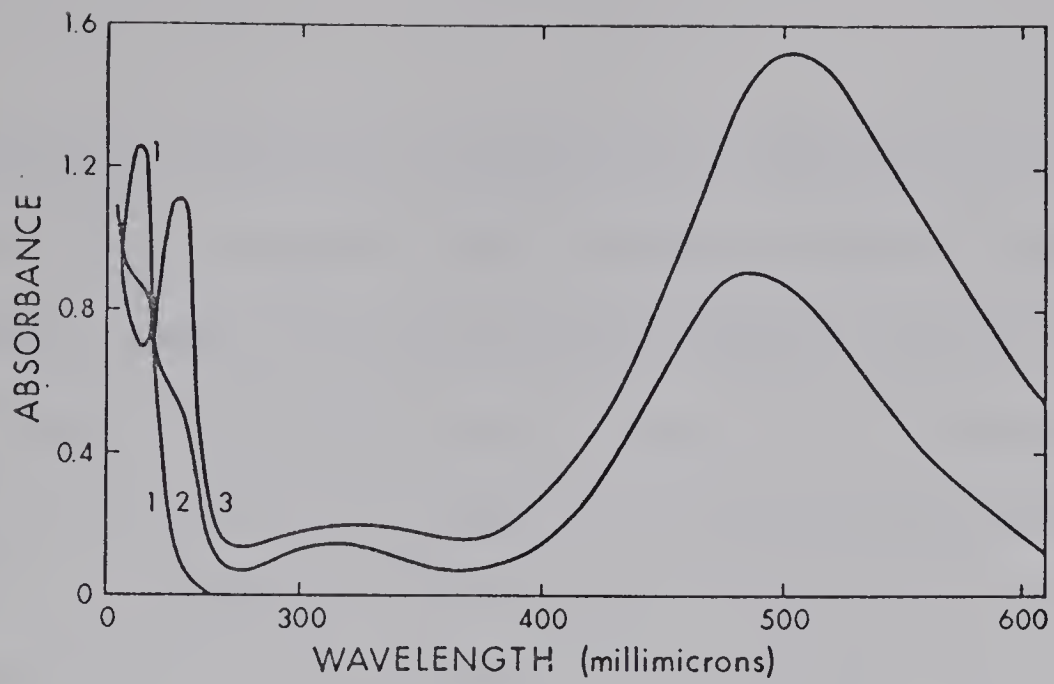


Figure 13. Ultraviolet-visible spectra of species present in titration of thiocyanate with 0.1M hydrated iron(III) perchlorate (Numbers refer to sampling points shown by arrows on Figure 12)



formation of a mixture of  $\text{Fe}(\text{SCN})_6^{3-}$  and  $\text{Fe}(\text{SCN})_5\text{OH}^{3-}$  species. Curves 1 to 6 in Figure 13 show ultraviolet-visible spectra of samples taken at the corresponding numbered points on the potentiometric titration curve of Figure 12. The absence of absorption maxima for the iron(II)-thiocyanate complexes in curves 1 to 3 indicate that no iron(II) species are present and therefore that no oxidation has taken place. Solutions of iron(III) perchlorate alone show maxima at 218, 252, 278, and 366 millimicrons while iron(II) perchlorate has one broad absorption at 205-215 millimicrons. Thiocyanate maxima occur at 198 and 234 millimicrons, while thiocyanogen does not absorb in this region. The absorptions at 250, 315, and 490-540 millimicrons in Figure 5 are attributed to  $\text{Fe}(\text{SCN}_x)^{3-x}$  species, where x is estimated to be 4 to 6.

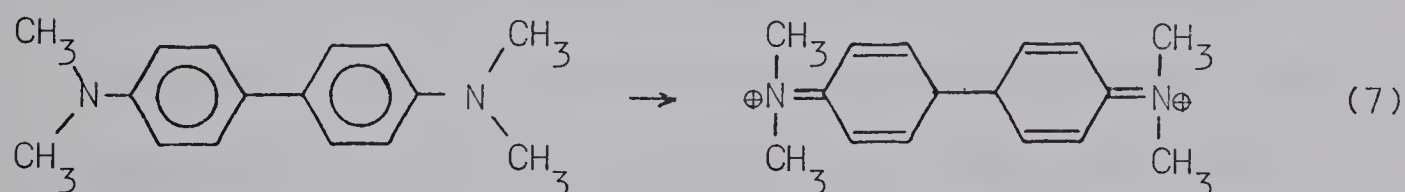
As the iron(III) to thiocyanate ratio is increased above 0.19, iron(III) reduction begins, as shown by the appearance of iron(II)-thiocyanate absorption peaks (Figure 13, curves 4 to 6). The end products of the oxidation are iron(II) and thiocyanogen. Thiocyanogen was identified by evaporating the titrated solution to dryness without allowing the temperature of the solid to rise above 0°C., then extracting the thiocyanogen with carbon disulfide. Evaporation of the carbon disulfide from the solutions gave free thiocyanogen. The behavior of this product was similar to that produced by bromine oxidation of silver



thiocyanate; at room temperature both polymerized to dark red parathiocyanogen,  $(\text{SCN})_x$ . Analysis: Calculated for thiocyanogen: C, 20.6; N, 24.1. Found for iron(III) oxidation product: C, 21.7; N, 23.3.

Complexation prior to oxidation is observed only when iron(III) is added to thiocyanate solutions. Reverse titrations with thiocyanate show only oxidation, as expected.

Aryl amines constitute another class of compounds which have been titrated with copper(II) and which are also susceptible to iron(III) oxidation. The product in many of these reactions contains one or more quaternary nitrogens. For example, tetramethylbenzidine undergoes the reaction:

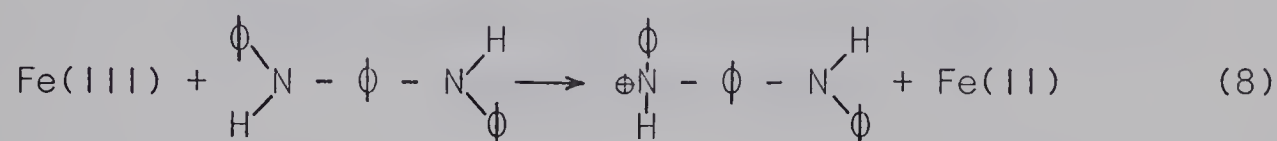


These reactions tend to be greatly influenced by the acid concentration. Excess acid in the iron(III) titrant solution may interfere by protonating basic sites on the compound being titrated, making it more oxidation resistant. Mechanisms for the homogeneous oxidation of diphenylamine, tetramethylbenzidine, and diphenylbenzidine are given by Kratochvíl and Zátka<sup>21</sup>.

One compound which reacted cleanly was N,N'-diphenyl-p-phenylenediamine (DPPD). Two well defined and reversible



breaks were observed (Figure 14a), similar to those found by Michaelis and Hill in 90% acetic acid<sup>3</sup>. Aqueous titrimetry cannot be used to determine this compound because of the insolubility of DPPD and the oxidation intermediates. The reaction steps are:



The semiquinone product of Equation 8 is stabilized in acid solution and gives a much sharper break if a few drops of 70% perchloric acid are added to the DPPD solution prior to titration. In this case the presence of excess acid is an advantage for it not only sharpens the breaks, but also increases the height of the second break at the expense of the first.

The phenothiazine compounds comprise another interesting class. These compounds contain a nitrogen and sulfur atom in a heterocyclic ring, and are fairly easy to oxidize because the oxidized form is stabilized by electron delocalization over the ring system. The parent phenothiazine is oxidized by iron(III) in two reversible one-electron steps (Figure 14b).





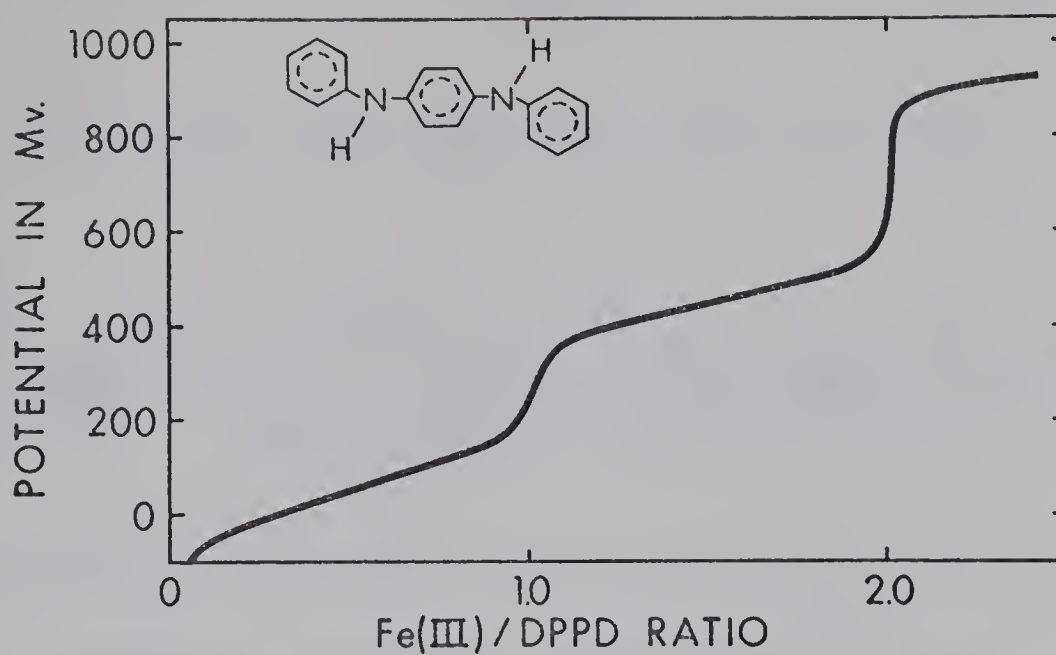


Figure 14a. Potentiometric titration of N,N'-diphenyl-p-phenylenediamine with 0.1M hydrated iron(III) perchlorate

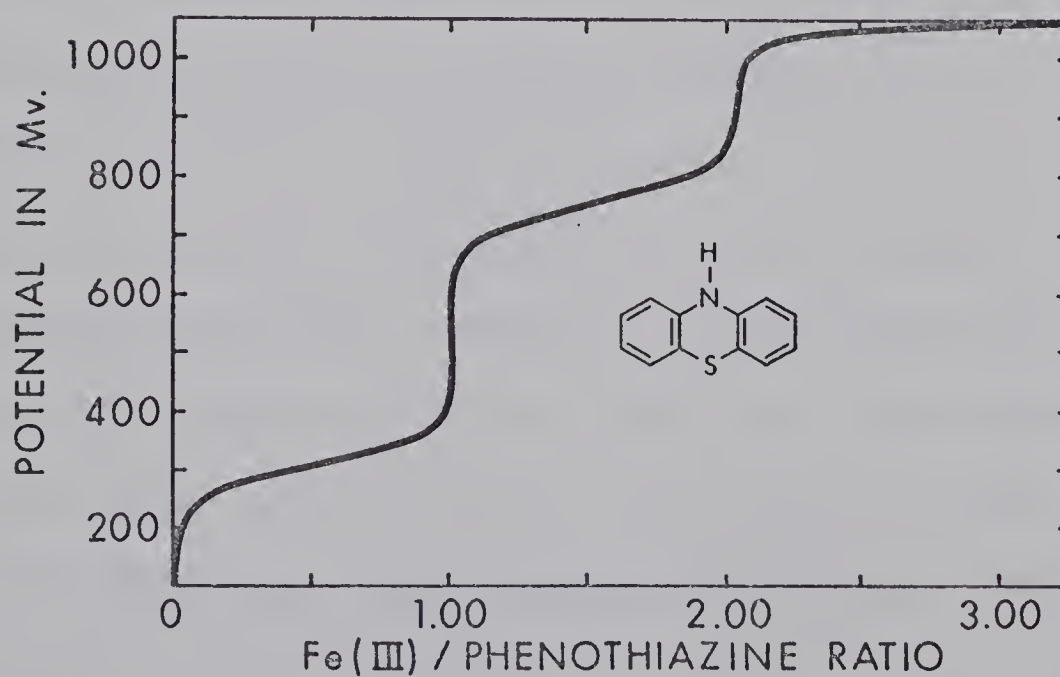
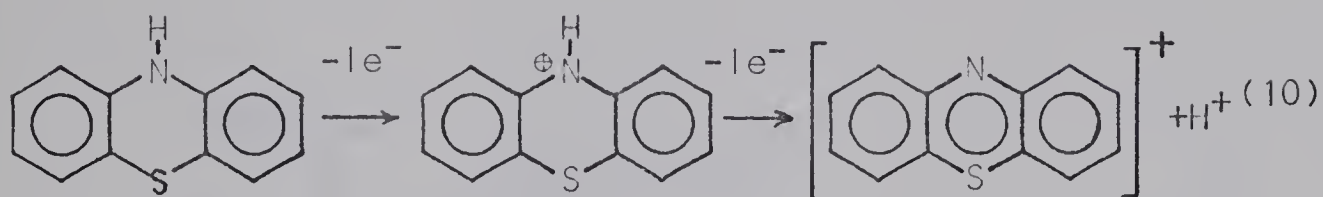


Figure 14b. Potentiometric titration of phenothiazine with 0.1M hydrated iron(III) perchlorate.



These steps have been shown electrochemically<sup>37</sup> to be:



Phenothiazine compounds, in which the proton on the ring nitrogen is replaced by an alkyl side chain containing a quaternary ammonium salt are widely used as tranquilizers and neuroleptic drugs. They are in general slightly harder to oxidize than the parent compound. A titration curve for the drug promazine perchlorate is shown in Figure 15. Other tranquilizer derivatives which were titrated included trimeprazine perchlorate, triflupromazine perchlorate, thioridazine perchlorate, prochloroperazine perchlorate, propiomazine perchlorate, thiopropazate perchlorate, and chlorpromazine perchlorate. However, the reactions were slow and in some cases the end points were small and unstoichiometric.

The last major class titrated in this survey consisted of compounds containing a double bonded sulfur atom. Some of these compounds have been titrated with copper(II) perchlorate with good results<sup>22</sup>. Hydrated iron(III) solutions, though powerful enough to oxidize several of these compounds, are not effective as oxidants in the presence of perchloric acid. Oxidation occurs through a zwitterion to form a disulfide



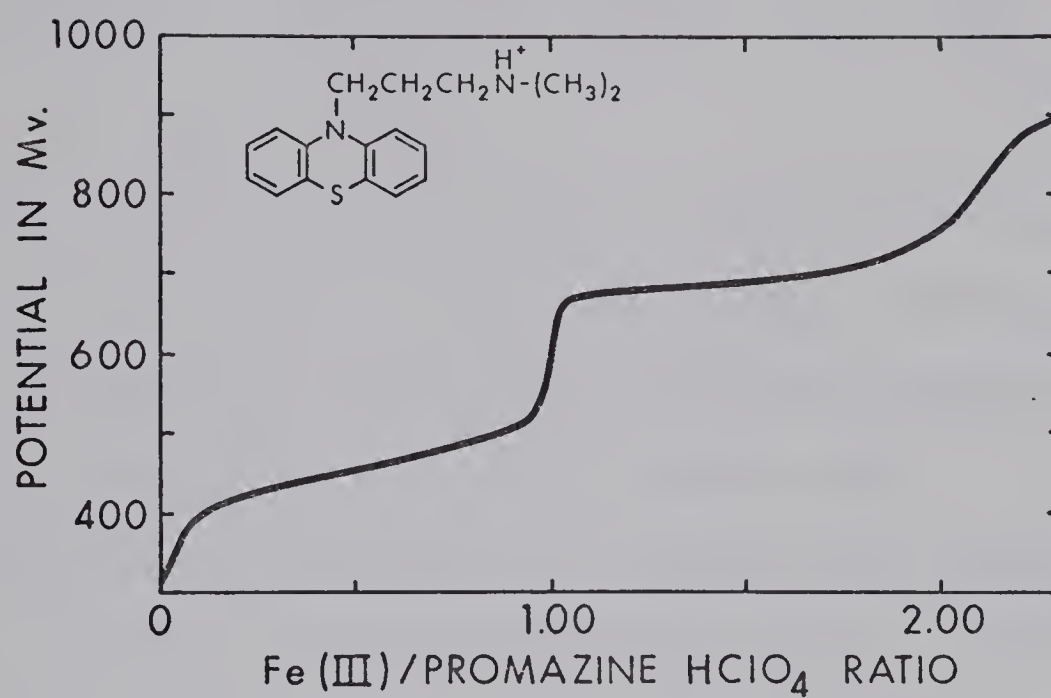
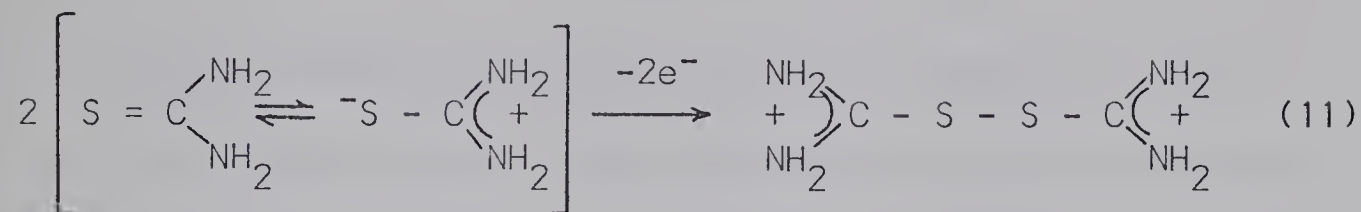


Figure 15. Potentiometric titration of promazine perchlorate with 0.1M hydrated iron(III) perchlorate



product; for thiourea<sup>22</sup> the reaction has been shown to be:



Perchloric acid protonates the sulfur in the enol form and blocks the site at which oxidation takes place. For this reason the breaks are drawn out and irreversible, though end points are reproducible at a given titration speed.

Thiourea is a good example of a compound which reacts through formation of resonance stabilized species. In this case both the zwitterion and the disulfide product are stabilized. Other compounds similar to thiourea, such as thioacetamide and thiocarbanilide, have less resonant stabilization but probably also react by the same mechanism. Compounds such as thiobenzanilide apparently do not give disulfide products that have sufficient resonant stabilization, so the disulfide breaks down to give free sulfur. These compounds gave obscure end points and no well-defined stoichiometry.





PART V.

SUMMARY

1. Anhydrous hexakisacetonitrile iron(II) perchlorate was prepared and used to electrochemically generate anhydrous iron(III) perchlorate in acetonitrile. Anhydrous iron(III) perchlorate could not be isolated from solutions of acetonitrile because of hydrolysis by traces of water.
2. The formal potential of the iron(III)-(II) couple in acetonitrile was determined to be 1.57 V vs. a silver, 0.01M silver nitrate in acetonitrile reference electrode at concentrations of  $2 \times 10^{-3}$ M for each iron species.
3. Formation constants for several iron(II) complexes in acetonitrile were measured spectrophotometrically. The log formation constant values obtained were:  $\text{FeCl}^+$ , 5.8;  $\text{FeBr}^+$ , 5.5;  $\text{FeI}^+$ , 4.3;  $\text{FeSCN}^+$ , 5.5; and  $\text{Fe(SCN)}_2 (\text{K}_2)$ , 3.7. Complexes of the  $\text{FeX}_2$  type were not detected for any of the halides.
4. Hydrated iron(III) perchlorate was investigated as an analytical oxidant in acetonitrile. Although the reduction potential of the iron(III,II) couple in the presence of water is much lower than the formal potential, it is still some 0.3 V higher than that of the copper(II,I) couple. Hydrated iron(III) was found to oxidize several classes of compounds, including benzidines, phenothiazines, and



ferrocenes. Iodide and thiocyanate are quantitatively oxidized to iodine and thiocyanogen, respectively.

Because of continuous hydrolysis and the apparent formation of a series of iron(III)-hydroxy complexes, the oxidizing power of solutions of iron(III) steadily decrease with time, and daily standardization with a compound of similar reduction potential to the compound being determined is necessary for accurate results.

5. Anion exchange membranes were found useful as dividers for coulometric work in acetonitrile because of low D.C. resistance, excellent barrier properties toward cations over a period of hours, and stability toward solvent attack.



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APPENDIX

Typical Data Collected for the Determination of a  
Formation Constant. Run #4 on the  $\text{FeBr}^+$  Complex

Iron(II) Solution:

Weight iron(II) perchlorate = 18.502 mg  
Weight of solution = 91.1565 g  
Density of solution = 778.5 g/liter

Tetrabutylammonium Bromide Solution:

Weight  $\text{Bu}_4\text{NBr}$  = 0.3000 g  
Weight of solution = 19.9280 g  
Density of solution = 778.5 g/liter

Injection Number	Injection Volume ( $\mu\text{l}$ )	Absorbance @ 265 $\text{m}\mu$
0		0.032
1	49.54	0.078
2	49.54	0.124
3	49.54	0.168
4	99.07	0.272
5	99.07	0.364
6	99.07	0.458
7	99.07	0.506
8	99.07	0.631
9	99.07	0.714
10	99.07	0.790
11	99.07	0.860
12	99.07	0.920
13	99.07	0.975
14	99.07	1.029
15	99.07	1.075



Typical Determination - Continued

Injection Number	Iron(II):Br <sup>-</sup> Ratio	Iron(II) Concentration ( $\times 10^4$ )	Bromide Concentration ( $\times 10^5$ )
1	20.53	3.153	1.536
2	10.26	3.152	3.071
3	6.84	3.150	4.604
4	4.10	3.148	7.670
5	2.93	3.145	10.73
6	2.28	3.142	13.79
7	1.87	3.140	16.84
8	1.58	3.137	19.88
9	1.37	3.134	22.92
10	1.21	3.132	25.96
11	1.08	3.129	28.99
12	0.98	3.127	32.01
13	0.89	3.124	35.03
14	0.82	3.121	38.05
15	0.76	3.119	41.06

Molar absorptivity (calculated by least squares) = 3121

Correlation coefficient = 0.999721

Average of formation constants =  $25.65 \times 10^4$

Log of average of formation constants = 5.409

Standard deviation of formation constants =  $3.16 \times 10^4$

Injection Number	Formation Constant ( $\times 10^4$ )	Log Formation Constant
8	27.11	5.43
9	24.09	5.38
10	22.41	5.35
11	24.23	5.38
12	30.42	5.48





# COMPUTER PROGRAM FOR 1:1 COMPLEXES

## CALCULATION FO FIRST FORMATION CONSTANT

SPECTROPHOTOMETRIC DATA LIGAND INJECTED INTO LARGE CONC. OF METAL ION

CARD 1 TITLE AND DATE (EX. TRIAL NUMBER 1 FE(II)-SCN SYSTEM DATE)

CARD 2 COLUMNS 1-10 MOLECULAR WT. OF METAL SALT

COLUMNS 11-20 WT. OF SOLVENT ADDED TO REACTION CELL IN GMS.

COLUMNS 21-30 DENSITY OF SOLVENT IN GMS./LITER

COLUMNS 31-40 MOLECULAR WT. OF LIGAND COMPOUND

COLUMNS 41-50 VOLUME OF LIGAND SOLUTION IN LITERS

COLUMNS 51-63 WT. OF METAL SALT

COLUMNS 64-76 WT. OF LIGAND

COLUMNS 79-80 NUMBER OF INJECTIONS

CARD 3 COLUMNS 1-5,6-10,ETC INJECTION VOLUME DEC. PT. 1 SPACE LEFT

CARD 4 COLUMNS 1-5 ABSORBANCE BEFORE INJ. DEC. PT. 3 SPACES LEFT

CARD 5 COLUMNS 1-5,6-10,ETC. ABSORBANCES DEC. PT. 3 SPACES LEFT

CARD 6 COLUMNS 1-10 MOLAR ABSORPTIVITY OF IRON(II) AT WAVELENGTH OF ABSORPTION OF COMPLEX.

CARD 7 ANOTHER DECK OR BLANK CARD

REAL MWMET,MWLIG,CMET(40),CLIG(40),INJ(40),TITLE(20),ABS(40),Z(40)

1, WT(40), CML(40), XCLIG(40), FC1(40), LFC1(40), XCMET(40), LWTAVE

2, LAVE, A(40), B(40), C(40), RATIO(40), X(40), Y(40), CABS(40), FE

3MAB, DIF(40)

30 READ(5,19,END=50)TITLE

READ(5,1)MWMET,WSOL,DSOL,MWLIG,VLIG,WMET,WLIG,NUM

READ(5,2)(INJ(I),I=1,NUM)

READ(5,61) ABO

READ(5,60)(ABS(I),I=1,NUM)

READ(5,62) FEMAB

L = NUM - 2

DO 500 N = 5,L



COMPUTER PROGRAM FOR 1:1 COMPLEXES --- Continued

```
DO 8 I =1, NUM
FCI(I) = 0
LFC1(I) = 0
8 CONTINUE
SUMA = 0
SUMB = 0
SUMC = 0
SUME = 0
SUMK = 0
SUMWT = 0
M = N + 1
201 CONTINUE
SINJ=0
DO 6 I=1, NUM
SINJ=SINJ+(INJ(I)/1000000.)
CMET(I)=(WMET/MWMET)/((WSOL/DSOL)+SINJ)
CLIF(I)=((WLG/MWLG)*SINJ)/VLIG)/((WSOL/DSOL)+SINJ)
Z(I)=ABS(I)-ABO
WT(I)=Z(I)/0.160
RATIO(I) = CMET(I) / CLIG(I)
DIF(I) = CMET(I) - CLIG(I)
IF(DIF(I)) 400, 401, 401
400 CABS(I) = Z(I)
GO TO 6
401 CABS(I) = Z(I) - FEMAB * DIF(I)
6 CONTINUE
112 SUMXY=0.0
113 SUMX=0.0
114 SUMY=0.0
```



COMPUTER PROGRAM FOR 1:1 COMPLEXES -- Continued

```

115 SUMX2=0.0
116 SUMY2=0.0
    DO 205 I = 1,N
        Y(I) = CABS(I)
        X(I) = CLIG(I)
205 CONTINUE
    DO 301 I = 1,N
136 SUMXY=SUMXY+X(I)*V(I)
137 SUMX=SUMX+X(I)
138 SUMY=SUMY+Y(I)
139 SUMX2=SUMX2+X(I)*X(I)
140 SUMY2=SUMY2+Y(I)*Y(I)
301 CONTINUE
142 SLOPE=(N*SUMXY-SUMX*SUMY)/(N*SUMX2-SUMX*SUMX)
143 YINT=(SUMY-SLOPE*SUMX)/N
        DELA = YINT
        IF(DELA) 420, 421, 421
420 DELA = - DELA
421 CONTINUE
        IF(DELA.LT.0.0001) GO TO 80
303 ABO = ABO + YINT
        GO TO 201
    80 CONTINUE
144 FACT=1./(N*(N-1.))
145 SY=FACT*(N*SUMY2-SUMY*SUMY)
146 SX=FACT*(N*SUMX2-SUMX*SUMX)
        R2 = SLOPE**2* SX/SY
        WRITE(6,20)TITLE
        WRITE(6,212)

```



COMPUTER PROGRAM FOR 1:1 COMPLEXES -- Continued

```

WRITE(6,213)
DO 214 I= 1,NUM
WRITE(6,215) I, RATIO(I), CMET(I), CLIG(I), CABS(I), WT(I)
214 CONTINUE
WRITE(6,210) SLOPE
WRITE(6,211) R2
EMABS = SLOPE
DO 302 I = 1,NUM
CML(I) = CABS(I) / EMABS
XCLIG(I) = CLIG(I) - CML(I)
IF (XCLIG(I)) 31,31,32
31 WRITE(6,102) I
SUME = SUME + 1
WT(I) = 0
GO TO 302
32 XCMET(I) = CMET(I) - CML(I)
FC1(I) = CML(I) / (XCMET(I) * XCLIG(I))
IF(FC1(I)) 501, 501, 502
501 SUMB = SUMB + 1
WT(I) = 0
GO TO 302
502 LFC1(I) = ALOG10(FC1(I))
SUMA = SUMA + FC1(I)
SUMK = SUMK + (WT(I) * FC1(I))
SUMWT = SUMWT + WT(I)
302 CONTINUE
AVE = SUMA / (NUM - N - SUME - SUMB)
IF(AVE.LE.0.0) GO TO 500
LAVE = ALOG10(AVE)
```





COMPUTER PROGRAM FOR 1:1 COMPLEXES -- Continued

```

WRITE (6,78) AVE, LAVE
WTAVE = SUMK / SUMWT
IF(WTAVE.LE.0.0.) GO TO 500
LWTAVE = ALOG10(WTAVE)
WRITE(6,77) WTAVE, LWTAVE
DO 9 I = M,NUM
  A(I) = AVE - FC1(I)
  B(I) = A(I) * A(I)
  C(I) = B(I) / (NUM - N - SUME - SUMB - 1)
  SUMC = SUMC + C(I)
9 CONTINUE
STD = SUMC ** 0.5
WRITE (6,79) STD
WRITE(6,23)
WRITE(6,24)
DO 76 I = M,NUM
76 WRITE(6,58) I, RATIO(I), FC1(I), LFC1(I)
500 CONTINUE
GO TO 30
50 STOP
20 FORMAT('1 DETERMINATION OF FIRST FORMATION CONSTANT FOR ',20A4//)
1 FORMAT(5G10.3,2G13.2,14)
2 FORMAT(14G5.1)
61 FORMAT(1G5.3)
60 FORMAT(14G5.3)
62 FORMAT(G10.0)
19 FORMAT(20A4)
212 FORMAT(2X,'INJ',3X,'METAL:LIGAND',6X,'IRON(II)',10X,'LIGAND',8X,'A
1BSORBANCE',5X,'WEIGHT')

```



COMPUTER PROGRAM FOR 1:1 COMPLEXES -- Continued

```

213 FORMAT(2X,'NUM',6X,'RATIO',7X,'CONCENTRATION',5X,'CONCENTRATION',1
19X,'FACTOR'//)
215 FORMAT(2X,12,5X,G10.4,2X,G15.6,3X,G15.6,5X,G10.4,2X,G10.4)
210 FORMAT('OLEAST SQUARE DETERMINED MOLAR ABSORPTIVITY = ',G12.5/)
211 FORMAT(1X,'CORRELATION COEFFICIENT
102 FORMAT(1X,'DATA POINT ',12,' DOES NOT COMPUTE')
77 FORMAT('OWEIGHTED AVERAGE OF FORMATION CONSTANTS = ',G12.6,6X,'
1LOG OF WEIGHTED AVERAGE = ',G12.6/)
78 FORMAT(1X,'AVERAGE OF FORMATION CONSTANTS
1,'LOG OF AVERAGE = ',G12.6/)
79 FORMAT(1X,'STANDARD DEVIATION FROM AVERAGE = ',G12.6)
23 FORMAT('O',5X,'INJ NUM',4X'MET:LIG',8X,'BETA 1',6X'LOG BETA 1')
24 FORMAT (18X,'RATIO'/)
58 FORMAT(9X,12,4X,G10.4,2X,G15.6,4X,G10.4)
END

```





**B29934**